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CAUSE AND PREVENTION OF KILN AND DRY-HOUSE SCUM AND OF EFFLORESCENCE ON FACE-BRICK WALLS

By L. A. Palmer

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CAUSE AND PREVENTION OF KILN AND DRY-HOUSE SCUM AND OF EFFLORESCENCE ON FACE-BRICK WALLS

BY

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Bureau of Standards

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By L. A. Palmer

ABSTRACT

To determine the sources of efflorescence, 288 "wallettes" were constructed of 32 different types of face brick, together with 4 types each of limes, Portland cements, and bricklayers' cements. Continuous tests extending over a period of six months were made with the wallettes and simultaneously with the brick. Seventeen types of face brick developing no efflorescence in individual tests on brick alone did develop such in the wallettes. The use of waterproofing compounds in mortar is discussed. A number of tests indicate that the stearates are the most effective of such waterproofing materials.

In order to reduce kiln scum and to render a brick safer from the standpoint of efflorescence, the following drier conditions should obtain: (1) The drier temperature should be relatively high; (2) there should be a fairly rapid circulation of air; (3) humidity should be as low as possible; (4) there should be a minimum of sulphur dioxide gas present; and (5) a minimum of mixing water should be used.

In the kiln the amount of sulphates in a finished brick are reduced by (1) passing through the water-smoking period (especially the temperature interval, 700 to 1,000° F.) as rapidly as possible; (2) maintaining a good draft during water smoking; (3) burning in a strongly reducing atmosphere, or (if this is undesirable) (4) extending the soaking time and (5) raising the soaking temperature.

Dry-house or fixed scum is essentially sodium and potassium sulphates melted at the brick surface. This can be overcome by rapid drying, burning in a reducing atmosphere, or by the use of barium salts.

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I. INTRODUCTION

The first aim of this investigation was to determine the causes of and remedy for efflorescence on face-brick walls. This necessarily involved the study of both brick and mortar and the contribution that each gave to this annoyance. After a year's study of wall efflorescence it was decided to broaden the scope of the investigation and include therein any condition which would tend to detract from the desired surface appearance of a face brick. This would necessarily include any condition tending to give a marred appearance to the brick surface as it is removed from the kiln, as well as those conditions which cause the accumulation of salts on the surface subsequent to the brick being placed in a wall.

In the literature there is some confusion in the use of the terms "efflorescence," "kiln scumming," and "dry-house scumming" of brick. In order to differentiate between these three terms, it is probably best to merely state the cause or source of each.

Efflorescence as herein considered is the accumulation of salts, usually sulphates, upon the outer surface of a wall of a building. Any material in a wall, from front to back, including the backing-up materials, may, and does in certain instances, contribute to this accumulation of salts on the outer surface. These salts may exist

in the mortar or in the brick or in both materials. They are brought into solution by water, carried to the surface of the wall, and deposited upon the evaporation of the water. While there are other sources of these salts, such as the soil at the base of the building, they are infrequent and have been given no particular attention in this investigation.

Kiln scum is caused by the formation of sulphates (for the most part soluble) on the surface of a clay body during the drying and burning processes. The gaseous combustion products of the sulphur from the fuel, in conjunction with the water added in pugging and with the water of hydration in the clay, during the burning period in the kiln convert such materials as calcium and magnesium carbonates to their respective sulphates. This reaction has been noted very frequently in the literature, and has been well authenticated by the researches of various workers in this field of ceramics.

Dry-house or "fixed" scum, as it is usually called, has been less well understood. Seger [1] was the first to define this type of scum. Face-brick manufacturers have attributed it to soluble salts in the clay rather than to salts formed during the burning and drying processes, and the data given in Part II are in agreement with this supposition. It has been found in plant practice that this scum first appears in the drier. Upon subsequent burning it tends to become "fixed" and, after reaching this condition, is not removable by a continued high temperature or by a reducing atmosphere as is the more common kiln scum.

1. PREVIOUS INVESTIGATIONS

The publications relating to these surface defects have been somewhat numerous. Seger[2] was first to assign to kiln scumming its real cause. Lovejoy[3] also mentioned this type of scum and attributed it to the combined action of sulphur dioxide from sulphur in the coal, together with the escaping water of hydration from the clay during water smoking upon certain components in the clay, which in the brick industry are known as "bases." Parmalee[4] presented a compilation of various opinions on the subject. Williams[5] found a method of reducing scumming on red-colored brick by the use of ferric chloride. Hoffman and Mostowitch[6] described the reduction of calcium sulphate by carbon monoxide. Staley[7] experimented with various salts of barium in preventing drier scum. Orton[8] has shown the behavior

[1] Collected writings, **1**, pp. 213, 313.
[2] Collected writings, **1**, pp. 213, 313.
[3] Lovejoy, Ellis, Trans. Am. Ceramic Soc.; also Burning Clay Wares, pp. 328–332; also Ohio Mining J., **17**, p. 34.
[4] Parmalee, C. W., paper given before the Indiana-Illinois division of the Am. Face-Brick Assoc. at its meeting in Chicago, Apr. 11, 1922.
[5] Williams, A. E., Trans. Am. Ceramic Soc., **27**, p. 764.
[6] Hoffman, H. O., and Mostowitch, W., Sprechsaal, **44**, p. 235.
[7] Staley, H. F., Trans. Am. Ceramic Soc., **17**, p. 200.
[8] Orton and Staley, Third report of the committee of technical investigation, N. B. M. A.; 1908.

of sulphur-iron compounds under various conditions of firing. The work of Jackson[9] is of particular interest. He has shown that the extent of sulphate formation in the kiln processes is not materially increased by increasing the concentration of sulphur dioxide in the kiln atmosphere tenfold.

The data obtained in the work at the bureau are here presented in three parts. Part I deals with the causes of efflorescence on face-brick walls and includes a study of tests with various mortars and face brick. Part II is concerned with variable conditions in the dry house and in the kiln that are involved in the formation of soluble sulphates in the brick during its drying period and includes also the results obtained in a study of the various factors that influence the rate of elimination of these salts at the higher temperatures reached during the burning process. Part III contains the results of a study of dry-house or fixed scum.

In this connection it will be remembered that, as mentioned above, previous investigations by workers in ceramics had definitely established the fact that sulphates are formed during the drying and burning processes. Numerous statements have also been made relative to conditions which tend to increase or decrease the extent of the sulphate formation. For the most part these statements were merely qualitative. In this investigation all of the various factors involved in the plant processes were studied quantitatively with respect to the part that each played in its relation to dry-house scum, kiln scum, and efflorescence on a wall.

PART I

I. EFFLORESCENCE ON FACE-BRICK WALLS

In order that efflorescence may be developed on a wall, the latter must be permeable to water and the salts in the materials in the wall must be soluble. Water may enter a wall and be forced upward by capillarity from the soil, or it may enter in the form of rain, melted snow, or by direct absorption from humid air.[10] Water added to the mortar materials at the time of mixing may also permeate a considerable portion of the wall. Any water which has so entered the wall dissolves any soluble salts, and the solution is then gradually carried outward to the exterior surface as evaporation proceeds.

In order to assign to each and every material in the entire wall, including all materials back of the visible face brick, its share of the efflorescence which, of course, appears only on the face brick, it would be necessary to make a very extensive investigation, covering a period of years. The layman who beholds only the visible salts on the outer wall may not consider any materials as contributing factors

[9] Jackson, F. J., J. Am. Ceramic Soc., pp. 154–173; March, 1926.
[10] McBain and Ferguson, J. Phys. Chem., 31 (4), pp. 562–594; 1927.

beyond those which he sees. In order to get the essential facts concerning the mechanism of the development of efflorescence, it was thought to be expedient to study only the materials, brick and mortar, as contributing causes. Whatever facts found with respect to intervening cement-mortar joints in the outer wall of face brick would apply also to any cement-mortar or concrete-mortar materials, or cement blocks in the back-up materials. Whatever the various commercial grades of lime as used in mortar contribute to the development of efflorescence on the facing would apply also to products in which such lime is incorporated anywhere in the backing.

In the panel tests, described in this part of the investigation, only face brick were used. Later, in Part II of this report, it will be seen that a minimum quantity of soluble salts must not be exceeded in a brick if the latter is to be considered safe from the standpoint of efflorescence. Any such figure applies equally as well to brick, to hollow clay tile, or to any other burned-clay product used as back-up materials in a wall. It will be shown further in Part II of the report that the amount of soluble salts in a clay body is diminished by hard burning and by special methods of burning during the period that the clay body is in the kiln. Generally speaking, face brick are harder burned than the softer brick and tile used in the back-up part of the wall. It would naturally follow, then, that any tendency on the part of the face brick to develop efflorescence as found in the investigation would be found to an equal and most likely greater extent in these softer burned clay materials.

In order to study the part that mortar materials as well as face brick play in the development of efflorescence on a wall, there were selected four types each of well-known and extensively used limes, Portland cements, and bricklayers' cements. There were also selected from various parts of the United States 55 different types of face brick.

The brick and mortar materials were used in test panels made as follows: Three brick of the same type were laid up, one above another, with intervening joints one-half inch in thickness of a mortar prepared from 1 volume of the limes or cements mixed with 3 volumes of standard Ottawa sand.

Two of such panels were constructed with each type of brick laid up with a given lime, Portland cement, or bricklayers' cement mortar. Each pair of panels constituted a single test. Twelve tests, or twenty-four panels, were made with each of the four limes and cements, thus bringing the total number of panels tested to 288. Each lot of 24 panels composed of different face brick and the same mortar is called a series.

After the panels were constructed they were allowed to set and dry on the floor of the laboratory for at least three weeks before being

subjected to the test for efflorescence. At the end of this time each pair of panels was set in a separate pan containing about 1 inch of distilled water. One panel of each pair was set vertically in the pan, the other being set horizontally. Water was added to the pans from time to time as required to replenish loss from evaporation. The tests were continued for a period of six months.

Simultaneously with these panel tests, individual tests for efflorescence were made with the face brick of the same types as those used in the panels. Six brick of each of the 55 types received were given such individual tests with no mortar materials present. Each lot of six brick, representing one manufacturer's product, was tested in a pan separate from the others. The brick were set vertically in the pan and in about 1 inch of distilled water, and the tests in all cases were continued for a period of six months.

Analyses were made for total soluble salts with representative samples of each of the 55 types of brick. For such analyses a half brick was taken in each case. This was finely ground and mixed. Two hundred grams of the powdered material were extracted with hot water until successive leachings when evaporated to a small volume showed no further trace of sulphates. The combined washings were first filtered and then evaporated to complete dryness and the residue weighed. To the residue there was added about 50 cm^3 of 18 per cent HCl. The solution was again evaporated to dryness, the same volume of 18 per cent HCl added to the residue, and the solution filtered. The filter paper, dish, and any residue were washed thoroughly with hot water. About two drops of concentrated H_2SO_4 were then added to the filtrate, which was then again evaporated to dryness, the SO_3 fumes being carefully driven off. The soluble salts were then weighed as anhydrous sulphates. It was noted that in most cases the weight of the residue from the first evaporation was usually the same as that obtained in the last evaporation, indicating that for the most part any soluble salts in brick are in the form of sulphates.

In Table 1 there are given the results of these analyses, the results of the individual tests made with the brick themselves not in contact with any mortar, and the results of the tests for efflorescence made with the panels.

Considering only those brick which, because of their low soluble-salt content, did not of themselves develop any noticeable efflorescence in the six months' test, some of the data of Table 1 by being rearranged show that in these severe tests the mortars contributed to the development of efflorescence on the panels.

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TABLE 1

A. PANEL TESTS WITH FACE BRICK AND PORTLAND CEMENT MORTARS

	Brick No.	Total soluble salts in brick	Efflorescence on brick alone	Efflorescence on panels
		Per cent		
Series No. 1-A, Portland cement No. 1.	9	0.05	No efflorescence developed during the 6 months' test	Noticeable efflorescence along mortar joints after 3 to 4 months.
	27	.13	Noticeable efflorescence developed within 2 weeks	Efflorescence very noticeable within 2 weeks.
	8	.14	Noticeable efflorescence developed after 1 month's duration of test.	Do.
	17	.07	No efflorescence developed during the 6 months' test	Efflorescence noticeable on dry ends of vertical panel after 2 months.
	3	.03	do	Small spots of efflorescence visible along mortar joint after 4 months.
	15	.04	do	Noticeable efflorescence on joints after 3 to 4 months.
	19	.06	Slightly noticeable at end of 6 months' test	Barely noticeable efflorescence on dry end of vertical panel after 4 months.
	16	.03	No efflorescence developed during the 6 months' test	Noticeable efflorescence on joints and adjoining edges of brick after 2 months.
	7	.13	Noticeable efflorescence developed after 1 month's duration of test.	Noticeable efflorescence within 1 month.
	13A	.12	Noticeable efflorescence within 3 weeks	Do.
	5	.04	No efflorescence developed during the 6 months' test	No efflorescence developed on these panels during the 6 months' test.
	2B	.06	Slightly visible efflorescence after 4 months	Noticeable efflorescence on upper dry corners and edges of brick after 4 months.
Series No. 2-A, Portland cement No. 2.	17	.07	No efflorescence developed during the 6 months' test	Noticeable efflorescence on upper dry portions of panels after 3 months.
	8	.14	Noticeable efflorescence after 1 month	Scumming very noticeable within 2 to 3 weeks.
	27	.13	Noticeable efflorescence developed within 2 weeks	Do.
	5	.04	No efflorescence developed during the 6 months' test	Noticeable efflorescence on upper dry ends of brick and mortar of vertical panel.
	18A	.09	Noticeable efflorescence after 1 month's duration of test	Noticeable efflorescence after 1 month.
	18B	.03	No efflorescence developed during the 6 months' test	Barely noticeable efflorescence along corners and edges, particularly on vertical panel.
	3	.03	do	No efflorescence developed on these panels during the 6 months' test.
	13A	.12	Noticeable efflorescence developed within 3 weeks	Middle brick of each panel coated after 1 month.
	9	.05	No efflorescence developed during the 6 months' test	Noticeable efflorescence along mortar joints and dry ends.
	2B	.06	Slight scum appeared on dry ends after 4 months	Noticeable efflorescence on dry ends of brick of vertical panel after 1 month.
	19	.06	Slightly noticeable efflorescence at end of 6 months' test	Noticeable white efflorescence on lower mortar joint, horizontal panel, after 1 month.
	7	.13	Noticeable efflorescence developed after 1 month's duration of test.	Noticeable efflorescence at end of 1 month.

Noticeable=Can be easily seen at a distance of a few feet.
Barely noticeable=Can be seen only upon a very close scrutiny.
Very noticeable=Can be seen across a 20-foot room.

TABLE 1—Continued

A. PANEL TESTS WITH FACE BRICK AND PORTLAND CEMENT MORTARS—Continued

	Brick No.	Total soluble salts in brick	Efflorescence on brick alone	Efflorescence on panels
		Per cent		
Series No. 3-A, Portland cement No. 3.	16	0.03	No efflorescence developed during the 6 months' test	Noticeable efflorescence on mortar joints at end of 1 month.
	1	.06	do	Do.
	19	.06	Slightly noticeable efflorescence at end of 6 months	Efflorescence noticeable on joints after 3 to 4 months.
	24	.05	No efflorescence developed during the 6 months' test	Barely noticeable efflorescence on edges of brick adjacent to joints after 3 to 4 months.
	3	.03	do	Small spots of efflorescence along joints after 4 months.
	8	.14	Noticeable efflorescence developed after 1 month's duration of test.	Noticeable efflorescence developed within 1 month.
	22	.03	No efflorescence developed during the 6 months' test	Barely noticeable efflorescence along mortar joints after 4 months.
	50	.11	Noticeable efflorescence developed after 1 month's duration of test.	Noticeable yellowish-brown efflorescence on brick within 1 month.
	2B	.06	Slight degree of efflorescence after 4 months	Efflorescence very noticeable after 4 months.
	18A	.09	Noticeable efflorescence developed after 1 month's duration of test.	Noticeable efflorescence developed within 1 month.
	18B	.03	No efflorescence developed during the 6 months' test	Noticeable efflorescence appeared within 3 to 4 months.
	4	.02	do	Spots of efflorescence along joints after 4 months.
Series No. 4-A, Portland cement No. 4.	24	.05	No efflorescence developed during the 6 months' test	Noticeable efflorescence along joints after 1 month.
	8	.14	Noticeable efflorescence developed within 1 month's duration of test.	Noticeable efflorescence on joints and brick within 1 month.
	9	.05	No efflorescence developed during the 6 months' test	Barely noticeable efflorescence along joints after 6 months.
	50	.11	Yellow efflorescence developed within 1 month	Noticeable yellowish-brown efflorescence on mortar and brick at end of 1 month.
	7	.13	Noticeable efflorescence developed after 1 month's duration of test.	Noticeable efflorescence developed within 1 month.
	21B	.03	No efflorescence developed during the 6 months' test	No efflorescence developed on these panels during the 6 months' test.
	25	.02	do	Small spots of efflorescence on joints on upper dry ends of vertical panel after 6 months.
	2B	.06	Slight degree of efflorescence developed after 6 months	Do.
	18A	.09	Noticeable efflorescence developed during first month of test	Barely noticeable efflorescence after 1 month; did not increase.
	18B	.03	No efflorescence developed during the 6 months' test	Noticeable efflorescence on upper dry ends of mortar joints of vertical panel.
	19	.06	Noticeable efflorescence at end of 6 months' test	Barely noticeable efflorescence after 1 month; did not increase.
	5	.04	No efflorescence developed during the 6 months' test	Noticeable efflorescence on joints within 1 to 2 months.

B. PANEL TESTS WITH FACE BRICK AND BRICKLAYER'S CEMENTS

Series No. 1-B, bricklayers' cement No. 1.	27	0.13	Noticeable efflorescence within 2 weeks	Noticeable efflorescence within 2 weeks.
	17	.07	No efflorescence developed during the 6 months' test	Efflorescence barely noticeable after 6 months.
	9	.05	do	No efflorescence developed on these panels during the 6 months' test.
	7	.13	Noticeable efflorescence after 1 month's duration of test	Noticeable efflorescence at end of 1 month.
	5	.04	No efflorescence developed during the 6 months' test	No efflorescence developed on these panels during the 6 months' test.
	19	.06	Barely noticeable after 6 months	Barely noticeable after 6 months.
	8	.14	Noticeable efflorescence after 1 month's duration of test	Noticeable efflorescence after 1 month.
	3	.03	No efflorescence developed during the 6 months' test	No efflorescence developed on these panels during the 6 months' test.
	6	.10	Noticeable efflorescence after 1 month's duration of test	Very noticeable efflorescence at end of 1 month.
	15	.04	No efflorescence developed during the 6 months' test	No efflorescence developed on these panels during the 6 months' test.
	16	.03	do	Do.
	13A	.12	Noticeable efflorescence visible after 3 weeks	Efflorescence noticeable within 2 to 3 weeks.
Series No. 2-B, bricklayers' cement No. 2.	17	.07	No efflorescence developed during the 6 months' test	Noticeable efflorescence within 1 month.
	19	.06	Barely noticeable efflorescence at end of 6 months	Do.
	16	.03	No efflorescence developed during the 6 months' test	Do.
	7	.13	Noticeable efflorescence developed after 1 month of test	Very noticeable efflorescence within 2 to 3 weeks.
	10	.10	do	Do.
	8	.14	Noticeable efflorescence appeared within 1 week	Very noticeable on vertical panel within 1 week; noticeable on horizontal panel after 1 month.
	14	.14	do	Do.
	5	.04	No efflorescence developed during the 6 months' test	Noticeable efflorescence within 1 month.
	27	.13	Noticeable efflorescence developed within 2 weeks	Noticeable on vertical panel, particularly joints, after 1 month; barely noticeable on horizontal panel.
	3	.03	No efflorescence developed during the 6 months' test	Noticeable efflorescence within 1 month.
	13B	1.10	Very noticeable efflorescence within 1 week	Very noticeable efflorescence within 1 week.
	13A	.12	Noticeable efflorescence after 3 weeks	Noticeable after 1 month.
Series No. 3-B, bricklayers' cement No. 3.	7	.13	Noticeable efflorescence developed during first month of test	Noticeable efflorescence developed within 3 weeks.
	10	.10	do	Noticeable after 1 month.
	16	.03	No efflorescence developed during the 6 months' test	Noticeable efflorescence within 1 to 2 months, particularly on joints of vertical panels.
	18B	.03	do	Do.
	13A	.12	Noticeable efflorescence appeared within 3 weeks	Efflorescence very noticeable after 3 weeks.
	19	.06	Barely noticeable efflorescence after 6 months	Noticeable efflorescence, particularly on joints and adjacent edges of brick, after 1 month.
	5	.04	No efflorescence developed during the 6 months' test	Do.
	3	.03	do	Do.
	8	.14	Noticeable efflorescence appeared within 1 week	Very noticeable efflorescence on entire surface of panels after 2 weeks.
	27	.13	Noticeable efflorescence appeared within 2 weeks	Spots of efflorescence noticeable within 1 to 2 weeks.
	17	.07	No efflorescence developed during the 6 months' test	Very noticeable efflorescence on joints and adjacent edges of brick.
	28A	.02	do	Do.

Noticeable=Can be seen at a distance of a few feet.
Barnly noticeable=Can be seen only on a very close scrutiny.
Very noticeable=Can be seen seross a 20-foot room.

TABLE 1—Continued

B. PANEL TESTS WITH FACE BRICK AND BRICKLAYER'S CEMENTS—Continued

	Brick No.	Total soluble salts in brick	Efflorescence on brick alone	Efflorescence on panels
		Per cent		
Series No. 4–B, bricklayers' cement No. 4.	5	0.04	No efflorescence developed during the 6 months' test	Barely noticeable efflorescence on upper dry ends of mortar joints of vertical panel after 3 months.
	19	.06	Barely noticeable efflorescence after 6 months	Noticeable efflorescence more or less on all mortar joints, less on brick, after 1 month.
	13A	.12	Noticeable efflorescence appeared within 3 weeks	Noticeable patches of efflorescence uniformly distributed after 3 weeks.
	3	.03	No efflorescence developed during the 6 months' test	Small spots of efflorescence barely noticeable on mortar joints within 1 to 2 months.
	17	.07	do	Do.
	16	.03	do	Noticeable efflorescence on upper dry ends of joints of vertical panel after 4 months.
	7	.13	Noticeable efflorescence developed during first month of test	Noticeable efflorescence on joints and upper dry surfaces of brick and mortar of both panels at end of month.
	9	.05	No efflorescence developed during the 6 months' test	Efflorescence on joints and adjacent edges of brick noticeable within 1 to 2 months.
	15	.04	do	Do.
	18B	.03	do	Do.
	8	.14	Appearance of noticeable efflorescence within 1 week	Do.
	27	.13	Appearance of noticeable efflorescence within 2 weeks	Noticeable efflorescence on both brick and mortar after 1 month.

C. PANEL TESTS WITH FACE BRICK AND LIME MORTARS

Series No. 1–C, lime No. 1.	1	0.06	No efflorescence developed during the 6 months' test	Noticeable efflorescence on upper dry portions of panels within 2 months.
	50	.11	Noticeable efflorescence developed during first month of test	Noticeable efflorescence on upper dry portions of panels after 1 month.
	3	.03	No efflorescence developed during the 6 months' test	No efflorescence developed on these panels during the 6 months' test.
	22	.03	do	Do.
	19	.06	Barely noticeable efflorescence after 6 months	Do.
	21A	.02	No efflorescence developed during the 6 months' test	Barely noticeable on dry ends after 4 months.
	12B	.02	do	No efflorescence developed on these panels during the 6 months' test.
	5	.04	do	Do.
	13A	.12	Noticeable efflorescence within 3 weeks	Noticeable efflorescence within 3 weeks.
	2A	.12	Noticeable efflorescence developed during first month of test	Noticeable efflorescence on upper dry portions of panels after 1 month.
	18B	.03	No efflorescence developed during the 6 months' test	Efflorescence barely noticeable on joints after 1 month.
	24	.05	do	Barely noticeable spots of efflorescence on brick after 6 months.

Series No. 2-C, lime No. 2.	24	.05	do	Barely noticeable small spots of efflorescence on dry surface of brick.
	10	.10	Noticeable efflorescence developed during first month of test	Noticeable efflorescence on brick and mortar after 1 month.
	4	.02	No efflorescence developed during the 6 months' test	Barely noticeable efflorescence on dry ends of vertical panel on brick and joints.
	1	.06	do	Do.
	21B	.03	do	Do.
	25	.02	do	Do.
	5	.04	do	Do.
	15	.04	do	Do.
	2B	.06	Noticeable efflorescence after 4 months	Noticeable efflorescence on dry surfaces of both panels after 1 month.
	19	.06	Noticeable efflorescence after 6 months	Do.
	3	.03	No efflorescence developed during the 6 months' test	No efflorescence developed on these panels during the 6 months' test.
	50	.11	Noticeable efflorescence developed during first month of test	Noticeable yellow efflorescence on brick developed within 1 month.
Series No. 3-C, lime No. 3.	31	.02	No efflorescence developed during the 6 months' test	No efflorescence developed on these panels during the 6 months' test.
	24	.05	do	Do.
	9	.05	do	Do.
	4	.02	do	Do.
	18B	.03	do	Do.
	19	.06	Noticeable efflorescence after 6 months	Noticeable efflorescence of dry end of vertical panel only after 4 months.
	2B	.06	Noticeable efflorescence after 4 months.	No efflorescence developed on these panels during the six months' test.
	7	.13	Noticeable efflorescence developed during first month	Noticeable efflorescence on both panels after 1 month.
	15	.04	No efflorescence developed during the 6 months' test	No efflorescence developed on these panels during the 6 months' test.
	5	.04	do	Do.
	20	.11	Noticeable efflorescence appeared within 2 weeks	Noticeable efflorescence on middle brick of both panels within 2 weeks.
	21B	.03	No efflorescence developed during the 6 months' test	No efflorescence developed on these panels during the 6 months' test.
Series No. 4-C, lime No. 4.	9	.05	do	Noticeable efflorescence along mortar joints of vertical panel within 1 month.
	21B	.03	do	Do.
	19	.06	Noticeable efflorescence appeared after 6 months	Efflorescence on upper dry portions of brick and mortar of both panels within 3 to 4 months.
	20	.11	Noticeable efflorescence after 2 weeks	Noticeable efflorescence after 2 weeks
	7	.13	Noticeable efflorescence developed during first month of test	Do.
	15	.04	No efflorescence developed during the 6 months' test	Barely noticeable efflorescence along joints of vertical panel only after 1 month.
	4	.02	do	Do.
	13A	.12	Noticeable efflorescence within 3 weeks	Very noticeable efflorescence on brick and joints after 1 month.
	12B	.02	No efflorescence developed during the 6 months' test	Barely noticeable efflorescence on upper dry surfaces of both panels after 3 to 4 months.
	24	.05	do	Barely noticeable efflorescence on mortar joints of vertical panel; none on horizontal.
	16	.03	do	After 3 to 4 months barely noticeable efflorescence on upper dry portion of vertical panel only.
	21A	.02	do	Do.

Noticeable=Can be easily seen at a distance of a few feet.
Barely noticeable=Can be seen only upon a very close scrutiny.
Very noticeable=Can be seen across a 20-foot room.

Brick that did not develop efflorescence in tests on brick alone	Efflorescence developed on panels of lime series	Efflorescence developed on panels of bricklayers' cement series	Efflorescence developed on panels of Portland-cement series
5	2	2, 3, and 4	2 and 4.
18A	1	3 and 4	2, 3, and 4.
25	2		4.
21B	2 and 4		
9	4	4	1, 2, and 4.
24	1, 2, and 4		3 and 4.
4	2 and 4		3.
18B	1	3 and 4	2, 3, and 4.
22			3.
3		2, 3, and 4	1 and 3.
1	1 and 2		3.
16	4	2, 3, and 4	1 and 3.
17		1, 2, 3, and 4	1 and 2.
15	2 and 4	4	
28A		3	
12B	4		
21A			

The total number of different types of brick used in the panels was 32. Of this number, 15 did and 17 did not develop noticeable efflorescence during the six months' tests made on the individual brick.

It is evident also from the table that whereas efflorescence in many cases developed on the panels of a certain brick and not on the brick itself when tested singly and alone, yet there are also many instances in the same series wherein efflorescence developed on one panel with a given lime or cement and did not develop on another panel of the same lime or cement, both panels being composed of different types of brick, each of which developed no efflorescence in the individual tests. Such, for example, are Nos. 1, 3, 22, 19, and 21A of the lime series No. 1. Brick Nos. 1 and 21A did not develop efflorescence when tested alone, whereas panels of these same brick developed efflorescence with lime No. 1. On the other hand, brick Nos. 3, 22, and 19 developed no efflorescence in the individual tests with brick, and neither was there developed any noticeable efflorescence on the panels in which these same brick were used together with lime No. 1. The only explanation that can be offered is that the tendency of each of the 100 brick of any one type to develop efflorescence was not the same and that a possible variation in soluble-salt content existed among the brick of any one type. This is altogether possible.

It may be concluded from the above data that both brick and mortar materials contribute to the development of efflorescence on a wall.

II. THE USE OF WATER-REPELLENT SUBSTANCES IN MORTARS

Theoretically, any possible contribution to wall efflorescence on the part of mortars may be prevented or decreased if the mortar joint could be rendered more impermeable to water. It is not possible to fill all of the voids, but it is possible that the presence of a certain substance or substances within the voids could lessen the passage of water due to capillarity. It is reasonable to assume that if little or no water can enter mortar materials, there can be no leaching out of salts therein to any appreciable extent.

An extensive study of water-repellent materials was not undertaken in this investigation owing to the fact that a more or less exhaustive study of such substances had already been made.[11] However, the work that had been done was not concerned primarily with possible methods of preventing efflorescence on a wall.

A relatively soft and porous type of brick was used throughout in all of the tests with the water-repellent materials. Excepting those tests wherein a cement was used which already contained the water-repellent substance, the mortars were made either with Portland cement No. 4 or lime No. 3 (both listed in Table 1) or mixtures of this cement and lime, together with standard Ottawa sand. The relative proportions of the mortar materials were always such that the volume ratio of cement to sand or of lime to sand was 1 to 3. In case both lime and cement were used in the mortar the volume ratio was 2 volumes of cement plus lime (in varied relative proportions to one another) to 6 volumes of sand. Excepting those trials made wherein a cement was used to which the water-repellent material had already been added at the factory, and excepting also those trials in which diatomaceous earth was substituted in considerable quantity by weight for sand, the amount of the compound used was either that as specified by the manufacturer, if it had been purchased on the market, or else, if it were not a material made solely for this purpose, an amount of it equal to 2 per cent by weight of the cement or of the lime or of the lime plus the cement was used.

The materials generally used to prevent or reduce the penetration of water into mortar may be divided into two classes:

1. Inert materials, such as clay or diatomaceous earth.
2. Water-repellent substances, such as oils and stearates of calcium, aluminum, etc.

[11] B. S. Tech. Paper No. 3, by P. H. Bates and Rudolph J. Wig.

1. Inert materials

Clays, 1A, 1B, 1C, 1D, and 1E.
Diatomaceous earth (No. 15, in Table 2).

2. Water-repellent substances

No. of compound	Composition and properties
2.	White powder, contains considerable volatile matter, burns with odor of resin. Contains potash, lime, and alumina and considerable of clay or shale.
3.	Grayish-white paste, most of compound is inert; clay or shale, considerable volatile. Burns with odor of resin.
4.	White powder. Chiefly calcium stearate or oleate.
5.	White paste. Ammonium stearate.
6.	Liquid emulsion. Sodium or potassium soap.
7.	White powder, calcium stearate.
8.	White paste, ammonium stearate.
9.	Gray paste. Some calcium stearate, oleate, or palmitate, and considerable of clay or shale.
10.	Mostly calcium stearate; some inert aluminum, and iron compounds present.
11.	Clear liquid, special for lime mortars. An oil, mostly volatile.
12.	Gum arabic.
13.	Glycerin.
14.	Dextrin.
16.	Medium-grade auto-cylinder oil.
17.	China-wood oil.
18., 19., 20.	Waterproof cement containing calcium stearate.
21.	Aluminum stearate prepared in the laboratory.

The water-repellent material was added directly to the measured volumes of the mortar materials in the amount as already specified. Distilled water was then added in an amount such that upon thorough mixing the mortar had the desired consistency and was thoroughly workable.

Six bricks laid up with the mortar, giving five mortar joints, constituted a panel. After being constructed the panel was allowed to set and dry on the laboratory floor for three weeks prior to beginning the test. After this length of time the panel was set in a shallow pan, the brick being parallel to the base of the pan. The lower brick was about half submerged in a saturated solution of sodium sulphate, which was poured into the pan upon beginning the test. For a period of six months the level of the solution of sodium sulphate was kept fairly constant, and observations were taken from time to time, noting any upward progress of the salt solution through the mortar joints. When penetration did occur the crystals of sodium sulphate, appeared upon the second, third, etc., brick from the bottom, according as the rate of penetration was slow or rapid. Table 2 gives a summary of the results obtained in these tests. Under the caption "Results" are listed the conditions of the panels after six months' continuance of this severe test.

TABLE 2

Compound	Number of panels	Mortar	Results
1A	1	Portland cement-sand	Salts did not penetrate first joint.
1B	1	do	Do.
1C	1	1 volume cement; 1 volume lime; 6 volumes sand.	Salts penetrated first joint and appeared on second brick.
1C	1	Cement-sand	Salts did not penetrate first joint.
1D	1	do	Do.
1D	1	1 volume cement; 1 volume lime; 6 volumes sand.	Salts penetrated first two mortar joints and appeared on third brick.
1E	1	Cement-sand	Salts penetrated first joint and appeared on second brick.
1E	1	1 volume cement; 1 volume lime; 6 volumes sand.	Salts penetrated first three joints and appeared on fourth brick.
1E	1	1½ volumes cement; ½ volume lime; 6 volumes sand.	Salts penetrated first joint and appeared on second brick.
2	1	Cement-sand	Salts did not penetrate first joint.
2	2	Lime-sand	Salts penetrated first joint and appeared on second brick.
3	2	Cement-sand	Salts did not penetrate first joint.
3	2	1 volume cement; 1 volume lime; 6 volumes sand.	Do.
4	2	Cement-sand	Do.
4	2	Lime-sand	Do.
5	2	Cement-sand	Do.
6	1	do	Do.
6	1	Lime-sand	Do.
7	2	Cement-sand	Do.
7	2	1 volume lime; 1 volume cement; 6 volumes sand.	Do.
8	2	Cement-sand	Do.
8	1	do	Salts penetrated first joint and appeared on second brick.
9	1	do	Salts did not penetrate first joint.
10	2	do	Do.
11	2	Lime-sand	Salts penetrated all five joints, covering entire panel.
12	2	Cement-sand	Salts penetrated first three joints, appearing on fourth brick.
12	1	1 volume cement; 1 volume lime; 6 volumes sand.	Salts penetrated all joints, covering the entire panel.
13	2	Cement-sand	Do.
13	2	Lime-sand	Salts penetrated first four joints, appearing on fifth brick.
14	2	Cement-sand	Salts penetrated first two joints, appearing on third brick.
14	2	Lime-sand	Salts penetrated first four joints, appearing on fifth brick.
14	2	1½ volumes cement; ½ volume lime; 6 volumes sand.	Salts penetrated the first three joints and appeared on the fourth brick.
15	2	1 volume cement; 3 volumes of sand and diatomaceous earth. Weight of earth equals 10 per cent of weight of sand.	Salts penetrated first two joints, appearing on third brick.
15	2	1 volume cement; 1 volume lime; 6 volumes sand and diatomaceous earth. Weight of earth equals 10 per cent of weight of sand.	Salts penetrated first four joints, appearing on fifth brick.
16	2	Cement-sand	Salts did not penetrate first joint.
16	2	Lime-sand	Salts penetrated first three joints, appearing on fourth brick.
16	2	1½ volumes cement; ½ volume lime; 6 volumes sand.	Salts did not penetrate first joint.
17	2	Cement-sand	Do.
17	2	1½ volumes cement; ½ volume lime; 6 volumes sand.	Do.
17	2	Lime-sand	Salts penetrated first two joints, appearing on third brick.
18	2	Special cement with compound already added-sand.	Salts did not penetrate first joint.
19	2	do	Salts penetrated to second brick.
20	2	do	Salts penetrated to third brick.
21	2	Cement-sand	Salts did not penetrate first joint.
21	2	Lime-sand	Do.

From the data of Table 2 it is evident that for the most part all of the compounds used tended to decrease the rate of penetration of the sodium-sulphate solution through the mortar joints. It is also

evident that the inert materials, such as clay and diatomaceous earth, did not entirely prevent penetration in all cases. Such materials as gum arabic, glycerin, dextrin, and china-wood oil are also more or less ineffective.

With one exception (No. 8, in which a cement-sand mortar was used) the use of ammonium stearate in a quantity equal to 2 per cent by weight of the cement, lime, or cement plus lime, if both were used, prevented any penetration whatsoever of the salt solution.

Nos. 4, 7, 9, 10, and 18 were entirely effective in all cases in preventing any penetration of the salt solution through the mortar joints. These compounds were for the most part calcium soaps, usually the stearate. Aluminum stearate (No. 21) is equally effective.

It is to be noted in these latter cases mentioned that the presence of the compound in the mortar prevents any penetration whatsoever of the salt solution through the mortar joints and regardless of whether it were a cement, a lime, or a mixture of lime and cement mortar. In a few of the other cases in which the stearates were not used it is indicated that the effectiveness of the compound in preventing penetration of the salt solution through the mortar joint tends to be diminished as lime is substituted wholly or in part for the cement. This, as noted, however, does not apply in those tests wherein the water-repellent compounds used were the stearates.

A wall in which these water-repellent materials have been used must not be considered as being thoroughly waterproof. Rain may penetrate through the face brick to the back-up materials, brick, tile, etc., take salts into solution in these materials, and then carry them back to the outer wall during the subsequent process of the drying of the wall. The purpose of the stearates is only to render less likely the contributing of the various mortars used in the entire wall to the development of efflorescence on the outer wall. It is further evident that in order for this condition to be realized the water-repellent substances must be used in all of the mortar in the wall, in the backing as well as in the mortar used with the face brick.

III. GENERAL CONCLUSIONS, PART I

1. From the results of 288 panel tests continued for a period of six months for the purpose of ascertaining the extent of contribution of mortar materials to the development of efflorescence on face-brick walls, it is concluded that the various limes, Portland cements, and bricklayers' cements used in this investigation, either with the face brick or in the back-up materials with the brick used in backing, as poured concrete, cement blocks, etc., did actually contribute to the development of such wall efflorescence.

2. It is further to be concluded that an admixture of either ammonium or calcium stearate to mortar materials in an amount equal

to 2 per cent by weight of the cement or of the lime or of the cement plus lime (if both are used) will tend to greatly reduce the extent to which the mortar materials contribute to the development of wall efflorescence.

PART II

I. SOLUBLE SALTS IN BRICK AS A SOURCE OF WALL EFFLORESCENCE AND OF KILN SCUM

1. CAUSES

There are two possible sources of the soluble salts existing in face brick which may be either visible on the surface when the brick are removed from the kiln and which are present as either dry-house or kiln scum or which may not be visible until climatic conditions have caused an accumulation of the salts on the surface after the brick have been placed in the wall, the latter occurrence being known as efflorescence. These sources, which have often been mentioned in ceramic literature, are:

1. Soluble salts existing in the raw clay.
2. Soluble salts which are formed during the drying and burning operations in the manufacture of brick.

2. SOLUBLE SALTS IN CLAY

The following analyses of clays are typical. The clays listed are representative of those used in various parts of the United States in the manufacture of face brick. Invariably the soluble salts present were sulphates. No other salts in any measurable quantity were found in clays during the investigation.

Clay	Water-soluble sulphuric anhydride (SO_3)	Clay	Water-soluble sulphuric anhydride (SO_3)
	Per cent		*Per cent*
1	0.14	6	0.02
2	.15	7	None.
3	.04	8	.11
4	.07	9	.07
5	.04	10	.02

The above data would indicate that efflorescence developed on a finished brick would be hardly likely to come from the soluble salts in the original clay.

It will be shown later in this report that the soluble salts in clay tend more to produce another annoyance, namely, dry-house or fixed scum, than they tend to cause efflorescence on a wall.

3. SOLUBLE SALTS FORMED DURING THE DRYING AND BURNING OF BRICK

Coal often contains appreciable quantities of sulphur, either free or combined as pyrite. Upon burning, sulphur dioxide (SO_2) is the gaseous combustion product of this element. It is well known that certain metallic oxides, notably oxides of iron, tend by their presence to accelerate the oxidation of sulphur dioxide to sulphur trioxide. Clay is abundantly supplied with such catalysts. Sulphur trioxide (SO_3), the anhydride of sulphuric acid, can attack such substances as calcium and magnesium carbonates ("bases"), converting the latter to their soluble sulphates. In addition to carbonates of lime and of magnesia, there are other "bases" which are convertible to water-soluble sulphates by the combined action of water vapor and SO_3. Siderite, a carbonate of iron, and rhodochrosite, a carbonate containing manganese, iron, and magnesium, occur frequently in clay. Pyrite is also often present in clay and, in addition to being a source of SO_3 in the kiln, may, under certain conditions, be partially oxidized to the sulphate, or, again, may react directly with the carbonates, converting the latter to soluble sulphates. Silicates of soda and potash are also decomposed during burning and may combine with the SO_3 to form soluble sulphates. In the presence of water vapor this reaction proceeds at a measurable rate. In the drier the water vapor present is that produced upon the evaporation of the water used in mixing. In the water-smoking process in the kiln, at temperatures higher than those used in drying, water is present in the atmosphere in the form of superheated steam. This water vapor is that lost by the clay in giving up its water of hydration or constitution.

4. FACTORS WHICH MAY AFFECT THE RATE OF SALT FORMATION DURING THE DRYING PROCESS

The formation of soluble sulphates by the combined action of water vapor and sulphur trioxide upon bases in the clay is subject to the ordinary laws of chemistry. From the latter it is known that a given reaction may be accelerated according as certain factors are controlled.

The reacting materials in the drier are the bases in the clay, sulphur trioxide (if the waste-heat system is used and the kilns have not been previously exhausted for a sufficient length of time), and water vapor. Theoretically, then, the extent to which sulphates are formed during the drying of the clay body would be affected by the quantity present of each one of these reactants. We know also that the factor, air circulation, is involved, as this affects the rate of drying and thereby alters the time taken for the drying process. The time taken for the drying process is itself a factor concerned, since

the extent to which a reaction proceeds is dependent upon the time if the reaction be not instantaneous. Temperature also plays a part. Usually the speed of a reaction is increased very markedly by a small increase in temperature. This, however, necessitates that all other factors remain constant. In drying brick if we increase the temperature, we should thereby decrease the time taken for drying, since the mixing water added is evaporated more rapidly the higher the temperature.

It is apparent, therefore, that a quantitative study of the many and involved variable conditions is necessary before any definite statement can be made concerning the relative importance of any one single variable.

5. FACTORS INVOLVED IN THE FORMATION AND SUBSEQUENT DECOMPOSITION OF SULPHATES IN THE KILN PROCESSES

As stated previously, water of hydration is lost by the clay during the initial stages of burning. If a coal containing sulphur is used, sulphur dioxide enters the kiln and is partially oxidized to the trioxide. The latter gas, in conjunction with the water vapor present, can react with the bases, as also previously described. This would be essentially a surface reaction, as would also be the formation of sulphates in the drier. The catalytic effect of the clay in increasing the formation of sulphates is augmented in the kiln by the relatively high temperature.

In addition to the concentrations and active masses of the reactants, sulphur trioxide, water vapor, and bases, there also must be considered certain other substances which affect the active masses of the reactants. These substances are air (with its oxygen), which is necessary in order that sulphur dioxide may be converted to the trioxide; carbon monoxide, which is a reducing agent tending to reduce a sulphate to a more easily decomposable sulphite; and carbon dioxide, which by its presence merely dilutes the gases, inhibiting the oxidation of sulphur dioxide. The concentrations of all of these influence more or less the extent to which sulphates may be formed.

In the kiln processes, besides considering the formation of the salts, their decomposition must also be borne in mind. F. J. Jackson [12] has given some very valuable data showing that as we approach the higher temperatures the salts formed during water smoking begin to decompose at a noticeable rate. The manufacturer is particularly desirous of knowing more or less definitely the temperature at which these various salts begin to decompose and how the rate of such decomposition varies with the temperature and other factors as well. To establish intelligent plant control, one must know quantitatively the effect of each variable condition upon the rate of formation of

[12] Jackson, F. J., J. Am. Ceramic Soc., pp. 154–173; March, 1926.

the sulphates and also upon the rate of decomposition of these sulphates as higher temperatures are reached.

Accordingly, a quantitative study of these various factors was made. The results of this study, given below, are divided into two parts. Under II there are given the results found in studying the drying operations, and under III are given the results found in varying the conditions during burning.

II. A STUDY OF DRYING OPERATIONS

1. EXPERIMENTAL

(*a*) Preparation of Samples for Test.—One clay was used throughout in all of the tests described. This clay was analyzed and found to contain less than 0.01 per cent of soluble sulphuric anhydride, 0.12 per cent of soluble and insoluble sulphur compounds reported as total sulphuric anhydride, 0.32 per cent of lime soluble in hydrochloric acid, and no magnesia soluble in this acid. From the standpoint of efflorescence and scumming, the clay was far superior to the average in so far as basic materials in a clay tend to produce these annoyances.

The samples put through the drying and burning processes were half bricks made from the clay described above. In making these samples for test two different procedures were followed: (*a*) Brick were made from the clay to which no bases were added; (*b*) brick were made from the clay with which 2 per cent of very finely powdered limestone had been very thoroughly mixed.

In all cases except where this particular variable was studied the quantity of mixing water was 14.3 per cent by weight of the clay.

(*b*) Laboratory Apparatus.—For the study of the drying processes the samples were placed in a Nichrome resistance oven, into which sulphur dioxide could be introduced at a definite and uniform rate of flow controlled by means of a needle valve and a flow meter in the delivery line. The flow meter was attached to a vertical scale, the smallest division on which was 1 mm. The flow of sulphur dioxide could be accurately controlled to an extent such that the oil level in the meter could not be observed by the eye to change during a test when the difference in level was 15 mm. This difference in pressure level maintained a concentration of 5 per cent of SO_2 in the oven when the difference in pressure level within the air-flow meter registered 40 mm. With the oil levels at these respective difference values the combined volume of air and sulphur dioxide delivered per minute was 2½ liters. A pressure-level difference of 40 mm in the air-flow meter was sufficient to deliver 2,400 $cm^3 \pm 100$ cm^3 per minute with a maximum variation in level of 2 mm. A pressure level of 15 mm in the SO_2 flow meter gave a very constant flow, delivering

125 cm^3 of gas per minute. Calculating the ratio of the two gases as mixed in terms of percentage by volume, the maximum variation, 100 cm^3, of air per minute would change the relative volume percentage of SO_2 in the mixture of gases by ± 0.2 per cent. The two flow meters, the one for air and the other for sulphur dioxide, were calibrated against one another by passing air through each into graduated cylinders filled with water and noting the rate of displacement of the water.

In order to attain a degree of accuracy in the control of the flow of gases when the concentration of SO_2 was 0.5 per cent, compatible with reliable results, it was necessary to be guided in setting the needle valve on the SO_2 cylinder to the proper position by counting the bubbles of gas escaping per minute or five minutes, etc., and checking this against the volume of air collected in a small graduated cylinder when air issued through the same flow meter and at the same "number of bubbles per minute" rate. Thus, 20 bubbles per minute represented 12½ cm^3 of gas. Mixing this with 2,500 cm^3 of air delivered per minute, the percentage by volume of sulphur dioxide is 0.5 per cent. By repeated checking of the number of bubbles of SO_2 delivered per minute after once carefully adjusting the needle valve, it was found that there was scarcely any variation in the rate of delivery of the SO_2. Any error would, therefore, be due to a change in the rate of air flow, which, as stated, was seldom as much as 100 cm^3 per minute.

The lower humidities were maintained by first passing the air through a series of wash bottles containing water held at a temperature necessary to give the desired degree of saturation. High humidity at temperatures near the boiling point of water was maintained by passing steam into the oven from another source, and thus not mixing it with the air until both gases had entered the drying chamber. This was done to avoid condensation in the line.

The relative humidity was obtained from the readings of two wet and two dry bulb thermometers.

2. METHOD OF PROCEDURE

The samples prepared according to the two procedures as mentioned in the "Description of the preparation of samples" were placed in the oven, which was already at the desired temperature and humidity for the particular test, and exposed therein for a definite length of time. Samples were removed at regular intervals, and analyses were made to find the percentage of water-soluble sulphuric anhydride which had been formed in the outer one-eighth inch of their surfaces during the definite length of time that they had been exposed to the known and controlled drying conditions.

Fifty grams of clay were scraped from the outer one-eighth inch of exposed surface of each sample. This was dried at 100° C. to constant weight, and 20 g were taken for analyses, which are given in Table 3. The 20-g sample was added to a liter of water, boiled for a few minutes, and filtered hot through an alundum cone. The clay was then further extracted repeatedly until the washings concentrated by evaporation to a small volume gave no further indication of the presence of soluble sulphates. The filtrate and collected washings were then made acid with HCl and evaporated to about 200 cm^3 and 25 cm^3 of saturated solution of barium chloride were added slowly to the boiling solution. The solution was then kept close to boiling temperature for at least 12 hours, the barium sulphate filtered off, and washed with hot water until no trace of chloride could be detected in the washings upon the addition of a drop of silver-nitrate solution.

TABLE 3

Sample No.	Added to clay (a=no bases added; b=2 per cent of $CaCo_3$ added)	Relative humidity of drier atmosphere	Concentration of SO_2 (by volume)	Flow of air and SO_2 (cm^3 per minute entering oven)	Temperature	Time of exposure of sample	Amount of mixing water used (by weight of clay)	Analyses (soluble SO_3 in outer exposed 1/8 inch of surface)	Mixing water lost during period of exposure	Remarks
		Per cent	*Per cent*		*°F.*	*Hours*	*Per cent*	*Per cent*	*Per cent*	
1A	b	25	0.5	2,500	212	5	14.3	0.22	--------	Conditions favorable for rapid drying.
1B	b	25	.5	2,500	212	8	14.3	.39	87.5	
2A	a	25	.5	2,500	212	5	14.3	.14	58.0	
2B	a	25	.5	2,500	212	8	14.3	.20	89.1	
3A	b	25	5.0	2,500	212	5	14.3	.77	63.5	Comparison of analyses of samples 1A, 1B, 2A, and 2B with analyses of samples 3A, 3B, 4A, and 4B shows the effect of increasing the concentration of SO_2 tenfold, all other factors being constant.
3B	b	25	5.0	2,500	212	8	14.3	1.13	91.0	
4A	a	25	5.0	2,500	212	5	14.3	.37	63.7	
4B	a	25	5.0	2,500	212	8	14.3	.52	95.0	
5A	b	80	.5	2,500	212	5	14.3	.71	21.3	Compare analyses of 1A and 1B with those of 5A and 5B, compare 2A and 2B with 6A and 6B, compare 3A and 3B with 7A and 7B, and compare 4A and 4B with 8A and 8B. By thus comparing these analyses, the effect of increasing the relative humidity threefold, keeping all other factors constant, is seen.
5B	b	80	.5	2,500	212	8	14.3	1.11	33.0	
6A	a	80	.5	2,500	212	5	14.3	.57	17.0	
6B	a	80	.5	2,500	212	8	14.3	.87	24.0	
7A	b	80	5.0	2,500	212	5	14.3	.91	13.8	
7B	b	80	5.0	2,500	212	8	14.3	1.27	23.5	
8A	a	80	5.0	2,500	212	5	14.3	.77	16.0	
8B	a	80	5.0	2,500	212	8	14.3	1.07	26.6	
9A	b	60	.5	2,500	212	5	14.3	.63	19.9	
9B	b	60	.5	2,500	212	8	14.3	.89	35.0	
10A	a	60	.5	2,500	212	5	14.3	.57	21.0	
10B	a	60	.5	2,500	212	8	14.3	.70	34.4	
11A	b	60	5.0	2,500	212	5	14.3	.87	17.5	
11B	b	60	5.0	2,500	212	8	14.3	1.23	32.0	
12A	a	60	5.0	2,500	212	5	14.3	.72	16.8	
12B	a	60	5.0	2,500	212	8	14.3	1.04	31.5	
13A	b	80	.5	2,500	165	5	14.3	1.46	5.8	Comparing analyses of samples 13A to 16 B, inclusive, with analyses of samples 5A to 8B, inclusive, the effect of lowering the temperature from 212° F. (boiling point) to 165° F., with all other factors constant, is noted. All other things being equal, the extent of salt formation is greater the lower the temperature.
13B	b	80	.5	2,500	165	8	14.3	1.64	8.5	
14A	a	80	.5	2,500	165	5	14.3	.85	6.2	
14B	a	80	.5	2,500	165	8	14.3	1.25	8.7	
15A	b	80	5.0	2,500	165	5	14.3	1.92	6.0	
15B	b	80	5.0	2,500	165	8	14.3	2.43	9.08	
16A	a	80	5.0	2,500	165	5	14.3	1.28	5.5	
16B	a	80	5.0	2,500	165	8	14.3	1.82	11.4	

88880°—28——4

TABLE 3—Continued

Sample No.	Added to clay (a=no bases added; b=2 per cent of $CaCO_3$ added)	Relative humidity of drier atmosphere	Concentration of SO_2 (by volume)	Flow of air and SO_2 (cm^3 per minute entering oven)	Temperature	Time of exposure of sample	Amount of mixing water used (by weight of clay)	Analyses (soluble SO_3 in outer exposed ⅛ inch of surface)	Mixing water lost during period of exposure	Remarks
		Per cent	*Per cent*		°*F.*	*Hours*	*Per cent*	*Per cent*	*Per cent*	
17A	b	25	0.5	2,500	165	5	14.3	0.84	20.0	
17B	b	25	.5	2,500	165	8	14.3	1.15	34.0	
18A	a	25	.5	2,500	165	5	14.3	.43	24.1	
18B	a	25	.5	2,500	165	8	14.3	.59	38.0	
19A	b	25	5.0	2,500	165	5	14.3	1.04	----------	
19B	b	25	5.0	2,500	165	8	14.3	1.79	33.5	
20A	a	25	5.0	2,500	165	5	14.3	.71	----------	
20B	a	25	5.0	2,500	165	8	14.3	1.12	35.0	
21A	b	80	.5	2,500	120	5	14.3	2.60	3.3	Samples 21A to 24B, inclusive, were exposed to conditions ideal for the extensive formation of salts. These conditions are high humidity and low temperature, resulting in very slow drying.
21B	b	80	.5	2,500	120	8	14.3	3.28	5.1	
22A	a	80	.5	2,500	120	5	14.3	1.37	2.8	
22B	a	80	.5	2,500	120	8	14.3	2.33	----------	
23A	b	80	5.0	2,500	120	5	14.3	2.47	2.4	
23B	b	80	5.0	2,500	120	8	14.3	3.46	4.1	
24A	a	80	5.0	2,500	120	5	14.3	1.89	1.8	
24B	a	80	5.0	2,500	120	8	14.3	2.70	3.2	
31A	b	25	.5	630	212	5	14.3	.67	37.0	Same conditions as in samples 1A and 1B, except draft is reduced 75 per cent.
31B	b	25	.5	630	212	8	14.3	.76	58.4	
31C	b	80	5.0	630	212	5	14.3	1.38	5.6	Same conditions as those obtaining in exposures of samples 7A and 7B except as to draft.
31D	b	80	5.0	630	212	8	14.3	1.63	11.4	
31E	b	80	5.0	630	212	12	14.3	2.14	28.1	
35E	a	80	5.0	630	212	5	14.3	1.02	7.0	Compare analyses with those of 8A and 8B. Draft alone was varied in the 2 cases.
35F	a	80	5.0	630	212	8	14.3	1.37	14.8	
32A	b	25	.5	2,500	212	5	7.0	.29	94.0	Compare analyses with those of 1A and 1B. Amount of mixing water alone is varied in the 2 cases.
32B	b	25	.5	2,500	212	8	7.0	.31	100.0	
33A	a	25	.5	2,500	212	5	7.0	.14	----------	Compare analyses with those of 2A and 2B. Amount of mixing water alone varied.
33B	a	25	.5	2,500	212	8	7.0	.19	----------	
34A	b	80	5.0	2,500	120	5	7.0	1.72	3.3	Compare analyses with those of 23A and 23B. Percentage of mixing water alone was varied in the 2 cases.
34B	b	80	5.0	2,500	120	8	7.0	2.93	7.7	

35A	a	80	5.0	2,500	120	5	7.0	1.35	---	Compare analyses with those of 24A and 24B. Percentage of mixing water alone is varied in the 2 cases.
35B	a	80	5.0	2,500	120	8	7.0	2.16	---	
36A	b	25	5.0	2,500	120	8	14.3	.58	94.4	Showing (from the analyses) that the formation of salts practically ceases with time as mixing water is entirely lost.
36B	b	25	5.0	2,500	120	12	14.3	.64	100.0	
36C	b	25	5.0	2,500	120	24	14.3	.66	100.0	
25A	b	80	.5	2,500	120	2	14.3	.72	.7	Temperature alone varied in these 3 tests. Bulk of salts were formed at the lower temperatures when drying was less rapid.
25B	b	80	.5	2,500	120 first 2 hours, 165 last 3 hours	5	14.3	1.29	10.4	
25C	b	80	.5	2,500	120 first 2 hours, 165 next 3 hours, 212 last 3 hours	8	14.3	1.94	18.2	
27A	b	80 first 2 hours, 55 last 3 hours	.5	2,500	120 first 2 hours, 165 last 3 hours	5	14.3	1.30	8.2	Simulating more or less actual conditions to which a brick may be exposed in plant procedures. Bulk of salts formed at the low temperatures and high relative humidities.
27B	b	80 first 2 hours, 55 next 3 hours, 25 last 3 hours	.5	2,500	120 first 2 hours, 165 next 3 hours, 212 last 3 hours	8	14.3	1.70	42.4	
26A	b	80	5.0	2,500	120	2	14.3	1.35	---	Bulk of salts were formed at the lower temperatures when drying was less rapid.
26D	b	80	5.0	2,500	120 first 2 hours, 165 last 3 hours	5	14.3	1.95	---	
26E	b	80	5.0	2,500	120 first 2 hours, 165 next 3 hours, 212 last 3 hours	8	14.3	2.30	20.0	
29A	b	80 first 2 hours, 60 last 3 hours	5.0	2,500	120 first 2 hours, 165 last 3 hours	5	14.3	1.68	12.0	
29B	b	80 first 2 hours, 60 next 3 hours, 25 last 3 hours	5.0	2,500	120 first 2 hours, 165 next 3 hours, 212 last 3 hours	8	14.3	1.90	48.0	
30A	a	80 first 2 hours, 60 last 3 hours	5.0	2,500	120 first 2 hours, 165 last 3 hours	5	14.3	.81	13.5	
30B	a	80 first 2 hours, 60 next 3 hours, 25 last 3 hours	5.0	2,500	120 first 2 hours, 165 next 3 hours, 212 last 3 hours	8	14.3	1.06	---	

3. DISCUSSION OF RESULTS

An interesting way of studying the data of Table 3 is to note the relation between the rate of evaporation of the mixing water and the rate of gain in soluble sulphuric anhydride in the exposed surface.

Consider the samples containing 2 per cent by weight of limestone and to which the same amount (14.3 per cent by weight) of mixing water was added, which were exposed for either five or eight hours in a drier atmosphere containing 0.5 per cent by volume of sulphur dioxide, be the humidity, temperature, etc., what it may, and compare the average gain in percentage of soluble SO_3 per hour with the average loss in per cent per hour of mixing water; for example:

Sample No.	Average gain of soluble SO_3 per hour	Average loss per hour of mixing water	Sample No.	Average gain of soluble SO_3 per hour	Average loss per hour of mixing water
	Per cent	*Per cent*		*Per cent*	*Per cent*
1A	0.04	6.5	5A	0.14	4.3
1B	.05	6.5	17B	.14	4.3
36A	.07	11.8	17A	.17	4.0
31B	.10	7.3	13B	.21	1.1
31A	.13	.74	13A	.29	1.2
9A	.13	4.0	21B	.41	.64
9B	.11	4.4	21A	.52	.66
5B	.14	4.1			

It will be noted that, with the exception of samples 36A, 31B, and 31A, the order of magnitude of the gain in percentage of soluble SO_3 per hour in the surface of the exposed sample increases more or less regularly as the rate of evaporation decreases. Hence it can be stated that, all other things being equal, the rate of conversion of bases to sulphates is diminished as the rate of drying is increased.

Considering separately each variable factor, it is evident that by increasing the concentration of sulphur dioxide in the drier atmosphere tenfold there is an increase, but by no means a corresponding increase, in the extent of sulphate formation in the brick surface. Samples 7A and 7B, exposed to an atmosphere containing 0.5 per cent by volume of SO_2, had slightly more of soluble SO_3 in their exposed surfaces than had samples 5A and 5B, exposed to an atmosphere containing 5 per cent by volume of SO_2. All conditions other than this one variable concentration of SO_2 were the same in the two tests. Obviously, if there were no SO_2 in the drier, there could be no formation of sulphates.

The relative importance of the various factors is illustrated by comparing, for instance, samples 21A and 21B, exposed at 120° F. at a relative humidity of 80 per cent and in air containing a sulphur dioxide concentration of 0.5 per cent by volume, with samples 7A and 7B, exposed at 212° F., the same humidity and with ten times the

amount of sulphur dioxide present. Of the two variable factors, temperature and SO_2 concentration, it is far more important to elevate the drying temperature than it is to reduce the SO_2 concentration from 5.0 to 0.5 per cent. Of course, it is really more desirable to have no SO_2 present; but of the two cases considered, the conditions obtaining in the case of samples 7A and 7B are more desirable than the conditions of exposure of samples 21A and 21B.

The relative importance of humidity is interlocked with that of temperature. A low relative humidity is of less advantage at 212° F. in reducing salt formation than is a low humidity at low temperatures. Similarly, high humidity at low temperatures tends far more to increase the formation of the sulphates than does high humidity at high temperatures. If samples 15A and 15B are compared with samples 19A and 19B, both sets of samples having been exposed to the same and more nearly average temperature, 165° F., and with all other variable conditions identical, it is seen that by decreasing the relative humidity from 80 to 25 per cent the absorption of SO_3 has been decreased 30 per cent (averaging the analyses). In this connection, note also that the rate of evaporation in the case of samples 17A and 17B, conditions 165° F. and 25 per cent humidity, is about the same as the rate of evaporation in the case of samples 5A and 5B, conditions 212° F. and 80 per cent humidity, all other conditions in the two cases being identical. It is observed also that the rate of sulphate formation in the clay surfaces is about the same in both cases.

Since the sulphur dioxide (SO_2) and sulphur trioxide (SO_3) can be taken into solution by the mixing water in the brick surface, the SO_2 being subsequently oxidized to SO_3, it is obvious that there will be less of such absorption and consequent oxidation in the case of dry pressed brick or with the use of a minimum quantity of mixing water. From a comparison of samples 34A and 34B with samples 23A and 23B it is seen that this variable factor is as important as any other.

By comparing the analyses of samples 31A and 31B with those of 1A and 1B and also the analyses of 31C and 31D with those of 7A and 7B it is noticed that the rate of air circulation, all of the other variable factors being constant, is another variable factor influencing the extent of the formation of sulphates, the slower draft being more favorable to salt formation.

The conclusions can therefore be briefly summarized. The optimum conditions from the standpoint of preventing the formation of sulphates in the drier are:

(*a*) There should be no sulphur dioxide in the drier, or, if such a condition is not attainable, the concentration of this gas should be reduced to a very low value. This would mean that it must be far less than 0.5 per cent.

(*b*) The temperature should be as high as possible considering other things, such as the possibility of developing cracks in the green brick.

(*c*) Simultaneously with a relatively high temperature there should be a rapid air circulation. A sluggish draft tends to increase the humidity at any given temperature.

(*d*) The humidity should be as low as possible. A rapid draft and relatively high temperature together tend to produce such a condition.

(*e*) There should be a minimum of mixing water used.

These data should be considered in plant practice more in their quantitative than in their qualitative aspects. There should be in every face-brick plant adequate facilities for measuring accurately and at frequent intervals all of these variable conditions. The above brief summary—(*a*) to (*e*)—is essentially a qualitative statement. Table 3 itself is a quantitative expression of these same facts and serves to show the relative importance of each variable condition.

4. OXIDATION OF SULPHUR DIOXIDE IN THE DRIER

The amount of sulphur dioxide (SO_2) combined as such in the clay surface and not subsequently oxidized to the sulphate during the period of exposure of the sample was also determined. If the filtrate obtained after extracting the clay sample is boiled with bromine, any sulphite present is oxidized to sulphate. A determination of the latter thus gives both the SO_3 present and the SO_2 as SO_3. Following are a few comparisons of total soluble SO_3 so determined with the SO_3 combined as such in the sample:

Sample No.	Period of exposure	SO_3 present as such	Total SO_3
	Hours	*Per cent*	*Per cent*
5A	5	0.71	0.85
5B	8	1.11	1.19
6A	5	.57	.59
6B	8	.87	.93
21B	8	3.28	3.49
22B	8	2.33	2.68
26A	2	1.35	1.94

In the case of the samples 5A, 5B, 6A, and 6B the temperature was 212° F., whereas samples 21B, 22B, and 26A were exposed at a temperature of 120° F. It is also to be noted that there is a greater difference between the amount of SO_3 and the total SO_2 and SO_3 in sample 26A exposed for only two hours than there is in any of the other samples. That SO_2 adsorbed or absorbed in the clay surface can be so completely oxidized is most likely due to the catalytic action of clay, even at these low temperatures, and may be due also in part to the relatively high concentration of the SO_2 on the imme-

diate surface of the clay. By the law of mass action this would tend to greatly increase the rate of formation of SO_3 according to the reaction:

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

It is obvious from the data of Table 3 that the samples to which limestone was added had a greater tendency to absorb and combine with the SO_3 than had the other samples. Several complete analyses, in addition to merely determining the amount of SO_3, were made with the water extractions of the samples. These analyses show that, with bases present, a considerable part of the sulphuric acid reacts very quickly with the bases to form sulphates, and that a smaller part of it remains as sulphuric acid at the end of the period of exposure than remains in the case wherein there are no appreciable quantities of such bases in the clay. Following are typical analyses which serve to illustrate this point:

Sample No.	Added to clay	$CaSO_4$	$MgSO_4$	$Fe_2(SO_4)_3$ $Al_2(SO_4)_3$ (calculated as $Fe_2(SO_4)_3$)	Na_2SO_4	K_2SO_4	Uncombined soluble sulphuric anhydride
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
21A	2 per cent limestone	1.58	0.51	0.10	0.39	0.21	0.94
21B	do	2.40	.66	.11	.34	.29	1.08
22A	Nothing	.54	.60	.09	.41	.22	.30
22B	do	.48	.71	.14	.39	.28	1.20

The reaction is essentially a surface one, as the following typical analyses of the interior of the samples show:

Sample No.	Soluble SO_3 in center	Soluble SO_3 on outer $\frac{1}{8}$ inch of surface
	Per cent	*Per cent*
7B	0.07	1.27
5B	.04	1.11

III. VARIABLE FACTORS INVOLVED IN THE FORMATION AND DECOMPOSITION OF SULPHATES DURING THE BURNING PROCESS

The variable factors which tend to affect both the rate of salt formation and of subsequent decomposition at the higher temperatures during the burning processes are:

1. Rate of air flow or draft.
2. Rate of approaching the soaking temperature.
3. Concentration of sulphur dioxide in the kiln atmosphere.
4. Extent to which the kiln atmosphere may be oxidizing.

5. Extent to which the kiln atmosphere may be reducing.
6. The soaking temperature.
7. The soaking time.
8. Materials in clay convertible to sulphates.

1. PREPARATION OF SAMPLES

All of the above variable factors, with the exception of No. 8, may be controlled more or less in plant procedures. In this part of the investigation three different methods of procedure were used in preparing the samples from the same clay described in Part II, 1, (*a*), under "Preparation of samples." These three procedures were:

1. Brick were made from the clay to which 2 per cent by weight of calcium carbonate had been added.

2. Brick were made from the clay to which 2 per cent by weight of natural pyrite had been added.

3. Brick were made from the clay without the addition of any bases.

The same amount of mixing water (14.3 per cent by weight of clay) was used in all cases.

2. LABORATORY EQUIPMENT

The samples were exposed for the tests in an electrical-resistance muffle furnace, the inner volume of which was approximately 2 cubic feet. The flow of the entering gases, air, sulphur dioxide, and both carbon monoxide and the dioxide, when the two latter were used, was controlled in the same manner as described in Part II, 2, laboratory apparatus used in the study of the variable conditions in the drying process. There was, however, no attempt here to control humidity, for obviously at temperatures far above the boiling point of water, relatively, humidity has very little meaning. The rate of flow of total gases is expressed in terms of the length of time taken to completely renew the furnace atmosphere one time. The concentration of any particular gaseous component of the mixture of gases refers to the actual percentage by volume of the total mixture in which that gas was present. The gases, mixed together in the concentration determined upon, entered the furnace at a definite rate of flow through a hollow fire-clay tube leading into the interior of the furnace. A small platinum-wound resistance unit encircling this tube served to preheat the entering gases.

Two calibrated platinum-rhodium thermocouples were used for temperature measurements. These couples were well covered by protection tubes and connected through the lead wires to a cold junction. Temperatures were recorded continuously by use of a recording potentiometer. During the course of the investigation the thermocouples were examined from time to time by the pyrometry section of the bureau to detect any departure from the original calibrations due to any possible action of the gases upon the platinum and rhodium metals.

3. METHOD OF PROCEDURE

The samples were dried to constant weight at 212° F. in an atmosphere free from sulphur dioxide. They were then placed in the electric furnace. The temperature was increased at a definite and uniform rate per hour, and the flow of gases meanwhile was regulated as already described. Samples made from the clay to which pyrite had been added were not burned along with the other brick containing no pyrite. As soon as the desired temperature was reached, or after a definite length of time according to the particular test, a sample was withdrawn. Fifty grams of the exposed surface were chiseled off to a depth not exceeding one-eighth of an inch. This was crushed and ground, and 20 g. were taken for an analysis. The analytical procedure was the same as that described in Part II, 2, with respect to the study of the drying process. Table 4 contains the results of these tests.

Table 4

FORMATION AND DECOMPOSITION OF SALTS DURING THE BURNING PROCESS (FURNACE ATMOSPHERE, OXIDIZING)

[Variable factor: Concentration of sulphur dioxide in the furnace atmosphere. Factors held constant: *Heating rate*, an increase of 30° F. in the furnace atmosphere each hour. *Draft*' flow of gases (air and sulphur dioxide only) such that the kiln atmosphere was completely renewed once each half hour]

Temperature when removed	Total time exposed	1. Brick made from clay containing 2 per cent by weight of limestone. Soluble SO_3 in outer ⅛ inch of exposed surface				2. Brick made from clay containing 2 per cent by weight of natural pyrite. Soluble SO_3 in outer ⅛ inch of exposed surface				3. Brick made from clay to which no bases were added. Soluble SO_3 in outer ⅛ inch of exposed surface.			
		(*a*) Sample exposed to 0.5 per cent of SO_2		(*b*) Sample exposed to 5 per cent of SO_2		(*a*) Sample exposed to 0.5 per cent of SO_2		(*b*) Sample exposed to 5 per cent of SO_2		(*a*) Sample exposed to 0.5 per cent of SO_2		(*b*) Sample exposed to 5 per cent of SO_2	
		Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3
° *F.*	*Hours*		*Per cent*		*Per cent*		*Per cent*		*Per cent*		*Per cent*		*Per cent*
705	24	2A	1.00			1A	0.63			3A	0.71		
860	30	2B	1.45	35A	1.54	1B	1.28	34A	1.60	3B	1.20	36A	1.27
930	32	5A	1.65			4A	1.58			6A	.94		
960	32			35B	1.88			34B	2.20			36B	1.34
1,000	35	5B	1.71			4B	1.91			6B	.97		
1,110	37	8A	1.88	8B	2.26	7A	1.63	7B	1.92	9A	.85	9B	1.28
1,200	40	11A	1.94	11B	2.01	10A	1.56	10B	1.82	12A	.74	12B	.88
1,300	44	14A	1.89	14B	2.18	13A	1.32	13B	1.68	15A	.52	15B	.74
1,420	48	17A	.75	17B	1.52	16A	.61	16B	1.24	18A	.41	18B	.52
1,500	50	20A	.46	20B	.92	19A	.20	19B	.66	21A	.23	21B	.38

[Variable factor: The soaking temperature and the soaking time. Heating rate: 30° F. per hour. Draft: Furnace atmosphere renewed completely once each half hour]

Soaking temperature	Soaking time	1. Brick made from clay containing 2 per cent by weight of limestone. Soluble SO_3 in outer ⅛ inch of exposed surface				2. Brick made from clay containing 2 per cent by weight of natural pyrite. Soluble SO_3 in outer ⅛ inch of exposed surface				3. Brick made from clay to which no bases were added. Soluble SO_3 in outer ⅛ inch of exposed surface.			
		(*a*) Sample exposed to 0.5 per cent of SO_2		(*b*) Sample exposed to 5 per cent of SO_2		(*a*) Sample exposed to 0.5 per cent of SO_2		(*b*) Sample exposed to 5 per cent of SO_2		(*a*) Sample exposed to 0.5 per cent of SO_2		(*b*) Sample exposed to 5 per cent of SO_2	
		Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3
° F.	*Hours*		*Per cent*		*Per cent*		*Per cent*		*Per cent*		*Per cent*		*Per cent*
1,745	12	26A	0.29	26B	0.18	25A	0.13	25B	0.18	27A	0.09	27B	0.17
1,800	2	23A	.31			22A	.14			24A	.09		
		23B	.24			22B	.11			24B	.08		
1,800	24	29A	.17	29B	.23	28A	.06	28B	.14	30A	.04	30B	.13
1,850	24	38A	.14	38B	.17	37A	.05	37B	.05	39A	.02	39B	.11

TABLE 4—Continued

[Variable factor: Draft; that is, flow of gases (air and SO_2). Heating rate: 30° F. per hour]

Temperature when removed	Furnace atmosphere completely renewed	1. Brick made from clay containing 2 per cent by weight of limestone. Soluble SO_3 in outer 1/8 inch of exposed surface				2. Brick made from clay containing 2 per cent by weight of natural pyrite. Soluble SO_3 in outer 1/8 inch of exposed surface				3. Brick made from clay to which no bases were added. Soluble SO_3 in outer 1/8 inch of exposed surface.			
		(a) Sample exposed to 0.5 per cent of SO_2		(b) Sample exposed to 5 per cent of SO_2		(a) Sample exposed to 0.5 per cent of SO_2		(b) Sample exposed to 5 per cent of SO_2		(a) Sample exposed to 0.5 per cent of SO_2		(b) Sample exposed to 5 per cent of SO_2	
		Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3
° F.			Per cent		Per cent		Per cent		Per cent		Per cent		Per cent
960	Once per half hour							34B	2.20			36B	1.34
960	Once per minute							42C	3.37				
1,000	Once per half hour					4B	1.91			6B	0.97		
1,000	Once per minute					42A	2.94			41A	1.07	41C	1.19
1,200	Once per half hour	11A	1.94										
1,200	Once per minute	40A	2.11										
1,300	Once per half hour	14A	1.89										
1,300	Once per minute	40B	1.94										
1,420	Once per half hour	17A	.75			16A	.61	16B	1.24	18A	.41	18B	.52
1,420	Once per minute	40C	1.08			42B	.88	42D	.94	41B	.45	41D	.61
1,500	Once per half hour	20A	.46										
1,500	Once per minute	40D	.65										

[Variable factors: The heating rate and draft]

Temperature when removed	Period of exposure	Heating rate per hour	Furnace atmosphere renewed	2. Brick made from clay containing 2 per cent by weight of natural pyrite. Soluble SO_3 in outer 1/8 inch of exposed surface				3. Brick made from clay to which no bases were added. Soluble SO_3 in outer 1/8 inch of exposed surface.			
				(a) Sample exposed to 0.5 per cent of SO_2		(b) Sample exposed to 5 per cent of SO_2		(a) Sample exposed to 0.5 per cent of SO_2		(b) Sample exposed to 5 per cent of SO_2	
				Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3	Sample No.	Soluble SO_3
° F.	Hours	° F.			Per cent		Per cent		Per cent		Per cent
900	15	60	Once per minute	46A	1.06			45A 45B	0.44 .51		
900	60	15	do	46C	2.68			45E 45F	1.24 1.18		
930	64	15	Once per half hour							45C 45D	1.16 1.20
930	32	30	do	4A	1.58					6A	.94
960	32	30	do			34B	2.20				
1,000	15	60	Once per minute	46B	1.38						
1,000	60	15	do	46D	3.26						
1,000	30	30	do	42A	2.94						

Temperature when removed	Period of exposure	Heating rate per hour	Furnace atmosphere renewed	Brick No. 1 (above)			
				(a) Samples exposed to 0.5 per cent of SO_2		(b) Samples exposed to per cent of SO_2	
				Sample No.	Soluble SO_3	Sample No.	Soluble SO_3
° F.	Hours	° F.			Per cent		Per cent
1,300	22	60	Once per minute			43A	1.73
1,300	22	60	do			43B	1.61
1,300	44	30	do	40B	1.91		
1,300	44	30	Once per half hour			14B	2.18
1,300	90	15	do	43C	2.26		
1,300	90	15	do	43D	2.34		
1,300	44	30	do	14A	1.89		

TABLE 4—Continued

FORMATION AND DECOMPOSITION OF SALTS DURING BURNING, ATMOSPHERE REDUCING

[Factors held constant: a, concentration of sulphur dioxide, 5 per cent; b, draft, furnace atmosphere completely renewed once each half hour; c, heating rate, 30° F. per hour]

[In the data following the reducing gas was admitted into the furnace either at the beginning of the burn or at some higher temperature. In the latter case it is to be understood that, prior to maintaining a reducing atmosphere, an oxidizing atmosphere (air 95 per cent by volume and SO_2 5 per cent by volume) was maintained. A concentration of sulphur dioxide equal to 5 per cent by volume of the total gases was maintained throughout, and this variable (kept constant) is therefore omitted under the caption furnace gases.]

Began reducing	Temperature at which sample was removed from furnace	Total time of exposure	Per cent by volume of total mixture of furnace gases			1. Brick made from clay containing 2 per cent of limestone		2. Brick made from clay containing 2 per cent of natural pyrite		3. Brick made from clay to which no bases were added.		Remarks
			Carbon monoxide	Carbon dioxide	Air	Sample No.	Soluble SO_3 in outer 1/8 inch of exposed surface	Sample No.	Soluble SO_3 in outer 1/8 inch of exposed surface	Sample No.	Soluble SO_3 in outer 1/8 inch of exposed surface	
	°F.	Hours	Per cent	Per cent	Per cent		Per cent		Per cent		Per cent	
	1,000	33	4	None.	91					49C	0.50	
	1,000	33	4	None.	91					49D	.42	
At start	1,110	40	5	90	None.	55A	1.18	56A	1.08			
	1,110	40	5	90.	None.	55B	1.34	56B	.97			
	1,300	44	5	90	None.	50A	1.35					
						50B	1.21					
	1,200	40	5	None.	90			48C	1.33			
1,000° F								48D	1.51			
	1,300	48	10	85	None.	51A	1.45					51A and 52A held for 4 hours at 1,300° F.
						52A	1.48					
	1,420	48	5	None.	90	47A	.78					
1,200° F						47B	.85					
	1,500	50	5	None.	90	47C	.68					
						47D	.59					
	1,520	50	5	None.	90			48A	.22			
								48B	.19			
1,000° F	1,580	52	5	None.	90					49A	.06	
										49B	.09	
	1,580	60	5	90	None.	53A	.35	54A	.08			Held at 1,580° F. for 8 hours.
						53B	.41	54B	.12			
1,580° F	1,580	60	5	90	None.	58A	.43					
						58B	.58					

1,000° F.	1,650	63	5	90	None.	52A	.07					Held at 1,650° for 8 hours.
						52B	.06					
1,650° F.	1,650	64	5	90	None.	57A	.11	60A	.07			
						57B	.19	60B	.11			
	1,650	62	2	93	None.			62A	.09			Compare analyses with those of 60A and 60B. Shows effect of varying concentration of carbon monoxide.
								62B	.11			
1,745° F.	1,745	66	5	90	None.	61A	.06					
						61B	.08					
	1,745	66	2	93	None.	59A	.12					Effect of reducing concentration of carbon monoxide. Compare analyses with those of 61A and 61B.
						59B	.09					

[In the following a concentration of only 1 per cent by volume of sulphur dioxide was maintained in the furnace atmosphere]

1,650° F.	1,650	62	2	97	None.	63A	0.06	64A	0.08			Ratio of carbon monoxide to sulphur dioxide, 2:1.
						63B	.05	64B	.10			

From comparisons of analyses of the interior of the brick with the analyses of the surface material as given in Table 4, it is apparent that, whereas the rate of formation of these sulphates on the surface is far more rapid than it is in the interior of the brick, the rate of decomposition of the salts that do form nearer to the interior is considerably less rapid than it is in the case of the sulphates near the surface. The following comparative analyses will illustrate this:

Sample No.	Temperature when removed	SO_3 at surface	SO_3 in interior
	°F.	*Per cent*	*Per cent*
8A	1,110	1.88	0.17
11A	1,200	1.94	.13
14A	1,300	1.89	.11
17A	1,420	.75	.15
20A	1,500	.46	.18
26A	1,745	.29	.15
29A	1,800	.17	.15
38A	1,850	.14	.10

The above comparative analyses refer to samples to which 2 per cent by weight of $CaCO_3$ (powdered limestone) had been added.

4. COMPOSITION OF THE SALTS FORMED

The following are typical analyses of the salts found by evaporation of the water extracts of the samples. These samples are among those which were exposed to identical conditions and hence the analyses illustrate the progressive elimination of these salts with increasing temperature. The percentage of sodium sulphate was obtained by difference, and any potassium sulphate present is considered as sodium sulphate. Any aluminum or manganese sulphates are calculated as ferric sulphate, $Fe_2(SO_4)_3$.

Sample No.	Added to clay	Temperature when removed	$Fe_2(SO_4)_3$	$CaSO_4$	$MgSO_4$	Na_2SO_4
		°F.	*Per cent*	*Per cent*	*Per cent*	*Per cent*
4B	2 per cent of pyrite	1,000	1.24	0.36	0.17	1.49
5B	2 per cent of limestone	1,000	.14	2.07	.21	.48
6B	Nothing	1,000	.08	.21	.11	1.29
16A	2 per cent of pyrite	1,420	.10	.17	.76	None.
17A	2 per cent of limestone	1,420	.07	1.02	.15	.07
18A	Nothing	1,420	.06	.49	.10	.02
25A	2 per cent of pyrite	1,745	.03	.10	.08	None.
26A	2 per cent of limestone	1,745	.04	.39	.06	None.
27A	Nothing	1,745	None.	.14	.02	None.

It is seen from these data that as the temperature is steadily increased the rate of elimination of calcium sulphate is less than that of the other salts and also that as 1,745° F. is reached the elimination of the alkali sulphates is complete. It is also seen, by comparing the analysis of sample 4B with that of 16A, that the elimination of iron sulphate is very rapid between the temperatures 1,000 and 1,420° F.

5. AMOUNT OF SOLUBLE SULPHATES NECESSARY TO RENDER A BRICK UNSAFE FROM THE STANDPOINT OF EFFLORESCENCE

The investigation developed the fact that the salt formation is essentially a surface reaction. The salts are formed and decomposed or eliminated there, and if this is incomplete the brick may be scummed or, if not scummed, may yet contain salts in sufficient quantity to develop efflorescence later on in a wall. To just what extent a face-brick manufacturer must reduce the amount of such soluble salts to know when he is within the margin of safety is desirable information. There are a number of factors which are involved. For example, a very small per cent of soluble magnesium sulphate will appear on a wall more quickly than an even larger quantity of calcium sulphate; also a very porous brick is more easily leached by water than a less porous one or one with a glazed surface.

The following data were obtained with brick having a minimum absorption of 10 per cent. Most of the samples had an absorption value of from 12 to 16 per cent. In obtaining these data the samples enumerated in Table 4, which after exposure were shown by analyses to have a low soluble salt content were used. Since also it was found, during this part of the investigation that the amount of salts in any sample from the beginning to the finish of a burn is usually greater on the surface, it is believed that any analysis for the purpose of foretelling what contribution a brick will make toward wall efflorescence should be made from the exposed surface of that brick. The sample for analysis need not include any material beneath one-eighth of an inch from the exposed surface. In the following description of tests the samples were kept standing in an inch of water for at least one month:

Sample No.	Soluble sulphuric anhydride in outer 1/8 inch of exposed surface	Efflorescence	Sample No.	Soluble sulphuric anhydride in outer 1/8 inch of exposed surface	Efflorescence
	Per cent			*Per cent*	
28A	0.06	None.	54A	0.08	Slight.
30A	.04	Do.	59B	.09	Distinct.
37A	.05	Do.	60A	.07	Slight.
37B	.10	Distinct.	61A	.06	None.
49A	.06	None.	63A	.06	Do.
52A	.07	Do.	63B	.05	Do.
52B	.06	Slight.	64A	.08	Distinct.

The above samples include those to which limestone and pyrite had been added to the clay, as well as those made without any addition of such bases. The results should therefore be very representative. The tests to develop efflorescence were most rigid, and the conclusion is that a brick containing 0.05 per cent or less of water-soluble sulphuric anhydride in its surface is fairly safe from the standpoint of efflorescence.

IV. GENERAL DISCUSSION, PART II

It is observed by studying the data of the first part of Table 4 that the rate of formation of sulphates in the surface of the brick is most rapid between the temperatures 700 and 1,000° F. The data of this part of the table are plotted and the formation and partial decomposition of the salts are represented by Figures 1, 2, and 3. In each figure curve 1 represents the formation and decomposition of salts in the surface of a brick exposed to an atmosphere containing 0.5 per cent by volume of SO_2; curve 2 represents the same thing as

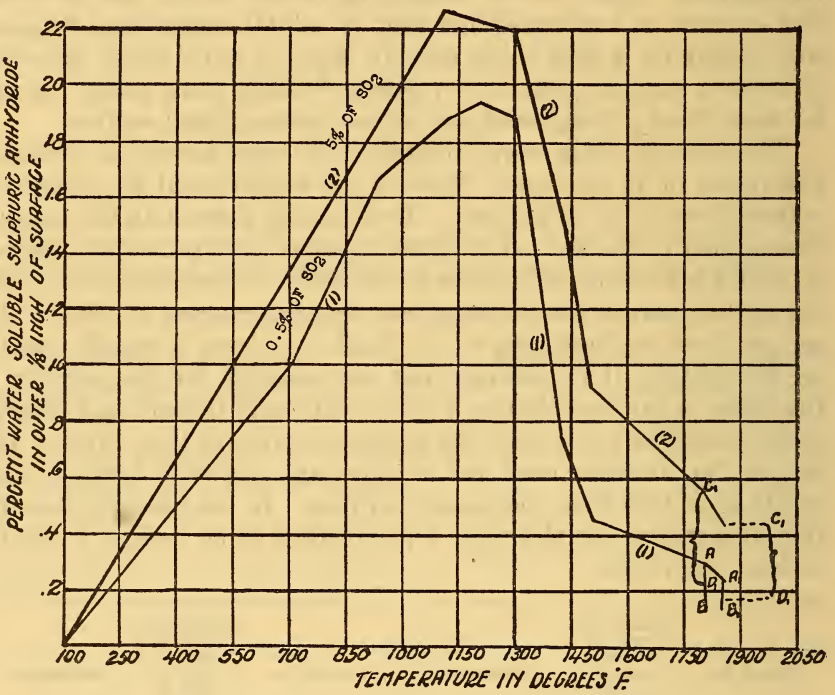

FIG. 1.—*Clay containing 2 per cent by weight of calcium carbonate*

happening in a kiln atmosphere containing 5 per cent by volume of SO_2; ab and a_1b_1 in curve 1 of each figure represents the decrease in per cent of water-soluble sulphuric anhydride in the exposed brick surface during a soaking period of 24 hours in an atmosphere of 0.5 per cent of SO_2 and temperatures of 1,800 and 1,850° F., respectively; cd and c_1d_1 represent the same thing as happening in each case at the two respective temperatures, but with the kiln atmosphere containing 5 per cent by volume of SO_2.

By comparing the samples 2A and 2B with 20A and 20B prepared according to procedure 1 with those prepared according to procedures 2 and 3 in the first part of Table 4, it is seen that as 1,300° F. is reached and passed the amount of water-soluble SO_3 in the exposed

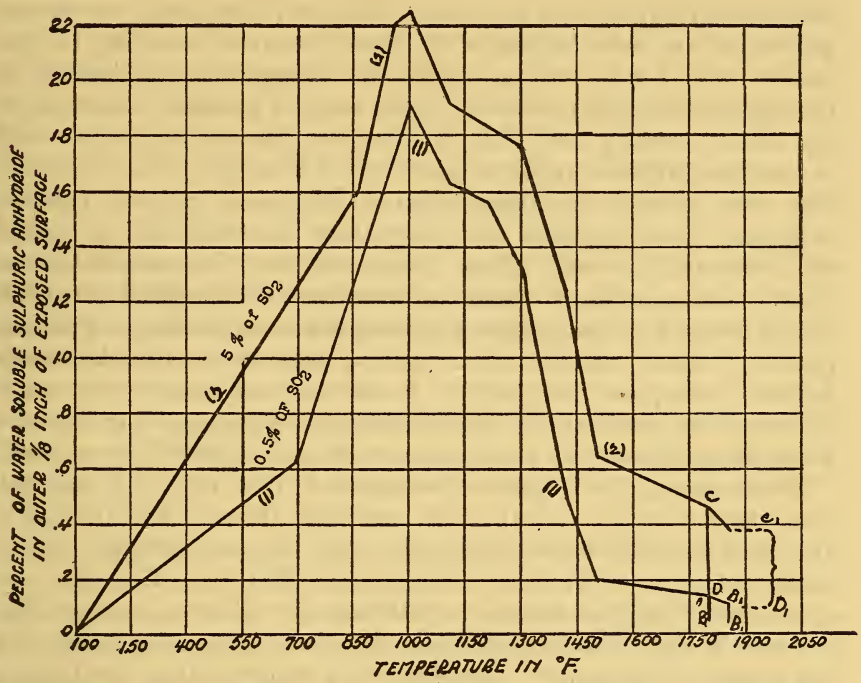

FIG. 2.—*Clay containing 2 per cent by weight of pyrites*

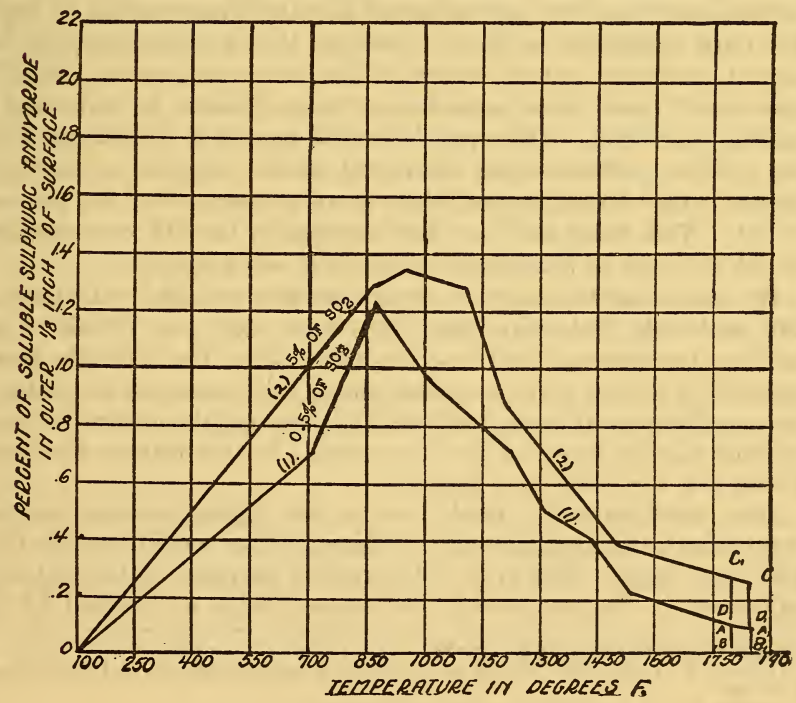

FIG. 3.—*Clay to which no bases were added*

surfaces is decreasing in all cases. However, elimination or decomposition of the salts begins in the brick prepared according to procedures 2 and 3 at or near 1,000° F., whereas the elimination or decomposition is not noticeable in the samples prepared according to procedure 1 until 1,300° F. is reached. In this connection it is well to note the published report of the work of Marschal [13] and of Cobb,[14] who have studied the dissociation of sulphates (notably calcium sulphate), both unmixed with any other materials and as mixed with clay and also with silica. They find that the temperature at which calcium sulphate begins to dissociate fairly rapidly is considerably lowered by the presence of the silica or of the clay. This can possibly explain the fact that calcium sulphate in the clay body begins to disappear as 1,300° F. is reached and passed, whereas it is known that pure calcium sulphate unmixed with any other material is not decomposed until a temperature of about 2,290° F. is reached.

By comparing the analyses of samples 8A, 11A, 14A, 17A, and 20A with those of 8B, 11B, 14B, 17B, and 20B, those of 7A, 10A, 13A, 16A, and 19A with those of 7B, 10B, 13B, 16B, and 19B, etc., listed in the first part of Table 4, it is apparent that increasing the concentration of sulphur dioxide tenfold does not cause a corresponding increase in the formation of salts. This is in good agreement with the report of Jackson.[15] However, it is believed that the limited amount of bases in the clay, convertible into sulphates, accounts more for this fact than does any failure of the law of mass action to apply. For data applicable to plant procedure it is not necessary to add more than 2 per cent by weight of limestone and pyrite. Such an amount of these bases is seldom, if ever, present in clay used in making face brick. However, it can be seen that practically all of the calcium carbonate was converted to the sulphate at the brick surface under favorable conditions in an atmosphere of 0.5 per cent of SO_2. This being the case, any increase in the SO_2 concentration would not tend to materially increase the salt formation.

By comparing the analyses of samples 29A and 38A with those of 29B and 38B, 28A with 28B, 30A with 30B, etc. (Table 4, the soaking temperature and soaking time being the variable factor studied), it is seen that the diminution of the amount of sulphates is, to a small extent at least, inhibited by increasing the concentration of sulphur dioxide from 0.5 to 5 per cent. In this respect the mass-action law certainly does apply.

One would naturally think that, as the higher temperatures are approached, the disappearance of the sulphates would become more and more rapid. However, if the rate of decrease of the sulphuric anhydride in the surface of the exposed brick as typified by the

[13] Marschal, Compt. Rend., **177**, p. 1300; 1923.

[14] Cobb, J. W., J. Soc. Chem. Ind., **29**, pp. 69, 250, 335, 399, 608, and 799; 1910. J. Phys. Chem., **23**, p. 38; 1926.

[15] Jackson, F. J., J. Am. Ceramic Soc., pp. 154–173; March, 1926.

analyses of samples 14A, 17A, 20A, 26A, 23A, 23B, 29A, and 38A, etc., is studied, it is seen that there is a far greater decrease as the temperature is increased from 1,300 to 1,500° F. than there is in the temperature range 1,500 to 1,754° F., etc., and that the latter in turn is very large in comparison with the diminution in soluble salts in the exposed surfaces which takes place as the temperature is increased to 1,800° F. and held at that temperature for 24 hours. The initial decomposition is the most rapid. This is true, in general, of reaction rates if we exclude autocatalysis. The initial masses of the sulphates being greater at the temperature at which decomposition begins than at any other time during the period of exposure, the rate of decomposition, considering this fact alone, would tend to be greater than at any other time. As the temperature is increased, any given mass of any salt would decompose more rapidly. However, it is seen that it is really more difficult to reduce the amount of soluble salts from 0.2 to 0.05 per cent than it is to reduce them in quantity from 2 to 0.2 per cent.

By comparing the analyses of samples 11A and 14A with those of 40A and 40B, etc. (Table 4, variable factor being draft), the following is to be noted: Increasing the draft thirtyfold, while maintaining all other variables constant, does not effect any decrease but rather does effect a slight increase in the extent of salt formation in the surfaces of the exposed samples prepared according to procedures 1 and 3. Comparing further the analyses of samples 4B and of 16A with those of 42A and 42B, etc., it is seen that, under the same conditions, increasing the draft thirtyfold results in a marked increase in the extent of salt formation in the exposed surfaces of brick containing pyrite in an appreciable quantity. This is due most likely to increasing the rate of oxidation of the pyrite, forming larger quantities of SO_2 and in turn SO_3 in a given time and bringing that gas into intimate contact with other bases as it passes out through the pores of the clay body. This is seen to be probable in view of the fact that increasing the draft did not so increase the extent of sulphate formation in the samples containing either no bases as added (3) or which contained limestone (1). It must not be concluded, however, that a rapid draft during water smoking has no advantages. A rapid draft during this period is of advantage if, and only if, it permits a more rapid rate of heating, thus decreasing the time of exposure during the formative period of the salts.

By increasing the rate of heating or by decreasing the time taken to reach that temperature at which the salts dissociate, the extent of salt formation is considerably lessened, as a comparison of samples 43A and 43B with sample 14B of Table 4, will show. By actually increasing the heating rate 100 per cent in the case of these samples the extent of salt formation is decreased by 22 per cent.

Increasing the draft during water smoking should render it safer to proceed rapidly through this period. Rapid heating between the temperatures 700 and 1,000° F. is especially desirable. In this temperature range the rate at which water of hydration is being given up by the clay is most rapid, and consequently such water in the form of vapor, acting in conjunction with sulphur trioxide, tends to accelerate the formation of salts.

It is evident from a study of that part of Table 4, descriptive of results obtained when the variable factors, soaking temperature and soaking time were studied (samples 30A, 39A, 37B, etc.), that a soaking temperature of 1,800 or 1,850° F. is sufficient to reduce the soluble salt content to a negligible quantity if the soaking period is sufficiently long. The soaking periods of these tests were considerably shorter than those used in actual plant procedures, but the results indicate more or less quantitatively the rate of decomposition of the salts when only a small amount of such exists at the soaking temperature. Also, these tests were so conducted that the samples were exposed to the most adverse conditions—that is, a high concentration of SO_2 in the kiln and relatively large quantities of bases in the clay—indicating that it may be possible to reduce to a negligible quantity the soluble sulphates in brick by heat alone, maintaining an oxidizing atmosphere. This, however, is most likely not the most economical procedure. There are greater possibilities of doing this with more economy by reduction if the use of such means will not interfere with other desirable qualities of the face brick, such as shade. A reducing atmosphere at high temperatures will in practically every case develop a shade different from that acquired by an oxidizing atmosphere at the same high temperature. It is questionable if there is an instance of the successful application in plant practice of a reducing atmosphere at a temperature considerably lower than the soaking temperature and yet high enough to decompose the salts. Such a condition, if it could be realized, would tend to rapidly diminish the sulphates, while at the same time there would be far less tendency to develop a shade different from that acquired in an oxidizing atmosphere. This implies, of course, that, following a period of reduction at from 1,600 to 1,700° F., the oxidizing atmosphere shall be resumed and continued throughout the entire soaking period.

It was found that the decomposition of the sulphates between 1,600 and 1,700° F. proceeds even more rapidly in a strongly reducing atmosphere than obtains in an oxidizing atmosphere at 1,850° F. The amount of residual soluble salts in samples 57A, 57B, 60A, 60B, 62A, and 62B, after these specimens had been exposed for eight hours to an atmosphere containing only carbon dioxide, carbon monoxide (the reducing agent), and sulphur dioxide, is seen to be about

the same as the residual salts in samples 37A, 37B, 38A, 38B, 39A, and 39B, burned for 24 hours at 1,850° F. in an oxidizing atmosphere. While the percentage by volume of carbon monoxide (5 per cent) is considerably higher than it is possible to have in the commercial-kiln atmosphere, the percentage by volume of sulphur dioxide is also correspondingly high. It should be possible in plant procedures to maintain the same volume ratio of the two gases (that is, 1:1), and it is observed that in the case of samples 62A, 62B, 63A, 63B, 64A, and 64B the diminution of soluble sulphates is sufficient to produce a material having little or no possibility of developing efflorescence. The latter specimens were burned in a reducing atmosphere containing 2 per cent by volume of carbon monoxide and 1 per cent by volume of sulphur dioxide, the remainder of the furnace atmosphere being carbon dioxide. It should be possible to maintain 2 per cent by volume of carbon monoxide in a kiln in plant practice, and 1 per cent by volume of sulphur dioxide would seldom be exceeded.

The fact that the extent of sulphate formation during water smoking was considerably lessened by the presence of a relatively small amount of carbon monoxide in the furnace atmosphere is somewhat surprising, considering the fact that the other gases were air and sulphur dioxide. Whether or not CO actually reduces SO_3 to SO_2 or whether the CO is preferentially absorbed at these temperatures on the surface of the clay bodies, thereby inhibiting the absorption of SO_3, is a matter for conjecture. It is a well-established fact, however, that in most catalytic gaseous reactions CO acts as a poison, inhibiting the desired reaction to a great extent. By banking the fire during water smoking and drawing the cold outside air over it in the fire boxes it might be possible to carry into the kiln a certain small amount of carbon monoxide during this period of the burn. At the same time one must not overlook the necessity of passing through this period of rapid salt formation as quickly as possible, and no operation designed to introduce carbon monoxide into the kiln atmosphere should prevent doing so.

V. GENERAL CONCLUSIONS, PART II

To render a brick safe from the standpoint of efflorescence and to diminish kiln scumming, the following conditions should obtain:

(*a*) *In the drier.*—Complete drying should be accomplished in the shortest possible period of time. Conditions that make this possible are a relatively high temperature, low humidity, the use of a minimum amount of mixing water, and good air circulation in the drying chamber.

The drying chamber should contain no gaseous combustion products of sulphur. If it is impossible to attain this condition in a plant where waste heat from the kilns is used, the concentration of the

sulphur dioxide in the dry house may be considerably decreased by exhausting the hot kiln for a length of time before connecting it to the drier.

(*b*) *In the kiln.*—The period of water smoking, and also the temperature range from 700 to 1,000° F., should be passed through as rapidly as conditions will permit. A rapid heating rate is rendered safer during this period if there is a good draft.

If burning in a reducing atmosphere is impracticable, the soaking temperature should be raised, if possible, and the soaking period extended.

If the desired shade may be acquired in a reducing atmosphere, the reduction may be carried out at the soaking temperature until draw trials show no evidence of scum.

It may be possible, in case the desired shade can not be attained in a reducing atmosphere maintained at the soaking temperature, to carry out reduction at a temperature of from 1,600 to 1,700° F., change to an oxidizing atmosphere and maintain such during the soaking period, and thereby have the desired shade, no scum, and a product safe from the standpoint of efflorescence.

In the drying and burning operations the formation of sulphates is essentially a surface reaction.

A brick which has 0.05 per cent or less of water-soluble sulphuric anhydride in the outer one-eighth inch of its exposed surface is fairly safe from the standpoint of efflorescence.

The rate of decomposition of sulphates in a brick surface is directly proportional to their respective masses. The decomposition rate becomes very slow after such decomposition has proceeded to an extent such that the quantity of soluble sulphuric anhydride in the brick surface is 0.2 per cent or less.

The rate of decomposition of the sulphates is increased to a considerable extent by the presence of a small percentage of reducing gas (carbon monoxide) in the kiln atmosphere.

PART III

I. DRY-HOUSE SCUM

1. DEFINITION

Among face-brick manufacturers the term "dry-house scum" refers particularly to that scum which is presumably due to soluble salts in the clay existing as such in the clay bank. This scum is not formed by the action of sulphur trioxide upon insoluble bases in the clay during the drying and burning processes as hereinbefore described.

The characteristic of dry-house scum, distinguishing it from ordinary kiln scum, is the great difficulty in removing it. It has a tendency to become fixed during burning, and after becoming so fixed a strong reducing atmosphere will scarcely affect it.

The salts in the clay tend to be concentrated upon the surface during the drying process, having been taken into solution by the mixing water. When the brick are removed from the drier, and prior to their entry into the kiln, these salts are often very noticeable on the surface that was exposed in the drier, and this fact accounts for the use of the term "dry-house scum."

2. SOLUBLE SALTS IN CLAY

Almost invariably the soluble salt content of clays is low. Clays have been leached for years by rainfall, and any considerable quantity of salts in the clay has been carried away for the most part. Ten clays used in making face brick and received from manufacturers operating in various sections of the United States were analyzed. The salts present were for the most part the sulphates of potassium and sodium, although sulphates of calcium and of magnesium were invariably present in the samples having the highest percentage of total soluble salts. The analyses gave the following data:

Clay No.	Water-soluble SO_3	Clay No.	Water-soluble SO_3
	Per cent		*Per cent*
1	0.14	6	0.02
2	.15	7	None.
3	.04	8	.11
4	.07	9	.07
5	.04	10	.02

With the exception of Nos. 1, 2, and 8, the amount of soluble salts is almost negligible.

3. EXPERIMENTAL PROCEDURE

By adding small quantities of salts to clay when trying to find the most effective barium treatment, it was found that in case the brick were dried slowly a glazed scum would appear and persist at 1,800° F. during the burning operation. In order to get enough of this scum, free from brick particles, for the purpose of determing its composition, the following method was used:

The anhydrous sulphates of calcium, magnesium, iron, manganese, sodium, and potassium were mixed in the following proportion: Potassium and sodium sulphates : iron sulphate : manganese sulphate : calcium and manganesium sulphates = 4 : 2 : 1 : 4. Using this salt mixture, the following tests were made:

No. 1. Clay, 90 per cent; salt mixture, 10 per cent. Samples were dried quickly (12 hours); then heated to 2,700° F. and held at this temperature for 3 hours.

No. 2. Clay, 90 per cent; salts, 10 per cent. Dried completely in 12 hours; heated to 2,290° F. and held for 30 hours.

No. 3. Clay, 90 per cent; salts, 10 per cent. Dried very slowly (1 week); heated to 2,290° F. and held for 30 hours.

No. 4. Clay, 70 per cent; salts, 30 per cent. Dried very slowly (1 week); heated to 1,830° F.and held for 24 hours.

No. 5. Clay, 70 per cent; sulphates, 30 per cent. Dried very slowly; heated to 2,290° F. and held for 30 hours.

No. 6. Clay, 50 per cent; sulphates, 50 per cent. Dried very quickly (12 hours at 212° F.); heated to 2,290° F. and held for 30 hours.

No. 7. Clay, 50 per cent; sulphates, 50 per cent. Dried very quickly (12 hours); heated to 1,650° F. and held at this temperature for 8 hours, meanwhile maintaining a strongly reducing atmosphere, 90 per cent carbon dioxide and 10 per cent carbon monoxide.

Table 5 gives the results of these tests.

TABLE 5

Trial sample No.	Surface after exposure	Soluble sulphuric anhydride in surface	Soluble sulphuric anhydride in interior	Remarks
		Per cent	*Per cent*	
1	Black, same as interior	1.04	0.80	No scum, no insoluble sulphur in any part of sample.
2	Black, no scum	None.	None.	Do.
3	Black, with spots of gray scum.	.14	None.	No insoluble sulphur.
4	Scum, white opaque	56.1	8.16	Surface scum, alkali and lime sulphates.
5	do	42.5	None.	Surface scum, mainly alkali sulphates.
6	Scum, white opaque and of considerable thickness.	53.9	None.	White scum consisting very approximately of Na_2SO_4, 34 per cent; K_2SO_4, 46 per cent; and $CaSO_4$, 20 per cent.
7	Brown to black, no scum	3.96	6.15	Sulphates not decomposed, chiefly calcium sulphate, some alkali sulphates, and none of magnesium, manganese, or iron.

The white scum on the surface of specimen No. 6 could be detached and was in quantity sufficient for a complete analysis. Figures 4 and 5 are photomicrographs of this dense and opaque surface scum. Figure 4 shows the surface of the specimen as magnified twenty times. Figure 5, a cross section of the specimen, magnified nine times, shows the layer of melted salts above the dark interior.

4. BARIUM TREATMENT

A considerable amount of work was done to find the most effective method of barium treatment. This point had already been studied quite extensively by other workers in ceramics, notably Staley, and the results of this investigation, in so far as it concerns this particular point, are in good agreement with his. For that reason it is not considered as necessary to tabulate here the experiments made with the various methods of using the barium compounds. It is well, however, to mention certain things and emphasize others in this connection.

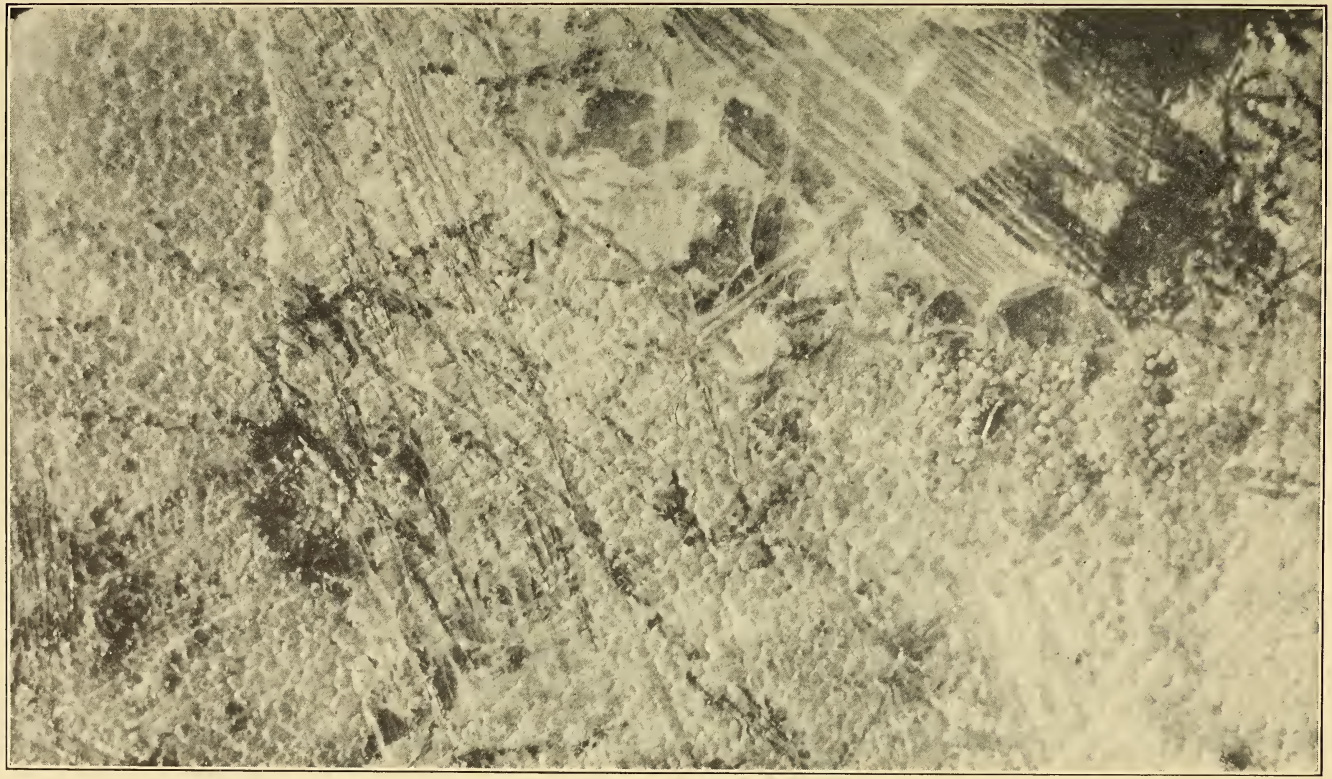

FIG. 4.—*Top view of fixed scum*

Magnified 20 times

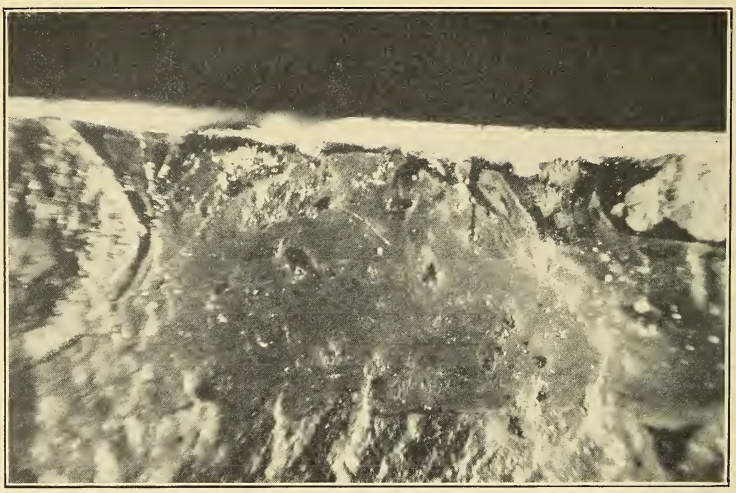

FIG. 5.—*Cross section of clay body showing layer of fixed scum on exposed surface*

Magnified 9 times

The results of this investigation point out very clearly the fact that, owing to the large percentage of salts formed in clay when a high-sulphur coal is being used, an excessive amount of barium carbonate would be required in such cases. The cost of the amount of barium carbonate necessary to prevent the formation of from 1 to 3 per cent of soluble sulphates is very excessive, and further than this, such an amount of barium carbonate present would tend to produce a light color in the final product.

Any barium salt, except barium sulphate, is to be recommended, therefore, for one purpose only, namely, to prevent dry-house scum.

Since dry-house scum, as above described, originates in the drying process, the soluble salts must be precipitated by the barium during pugging, so that they will not accumulate on the surface during drying. A soluble barium salt, therefore, is to be recommended, and an excess of such is to be avoided. The addition of an amount of sodium carbonate equal in weight to one-fourth of the theoretical weight of barium chloride, together with the theoretical amount of barium chloride calculated from analyses of the clay, has been found to be very satisfactory. Any excess of barium chloride remaining after the reaction to form insoluble barium sulphate will be converted to barium carbonate, and any excess of sodium carbonate is easily decomposed, the oxide forming silicates. Other and equally effective methods of treatment are:

The theoretical amount of barium fluoride, based upon the amount of sulphates in the clay.

The theoretical amount of barium hydrate.—Although the more soluble salts of barium are more expensive than the barium carbonate, it is possible to use considerably less of them than of the carbonate, but with greater effect. Furthermore, in barium fluoride and hydrate the amount of available barium is greater than that in other salts of barium.

II. CONCLUSIONS, PART III

Dry-house scum (so called in the plant) is composed chiefly of the melted sulphates of sodium and potassium on the exposed surface of a brick. It is caused by soluble alkali sulphates in clay and originates in the dry house. It may be overcome by (*a*) rapid drying; (*b*) barium treatment; and (*c*) a reducing atmosphere in the kiln, held at a temperature lower than the melting point of sodium sulphate; that is, a strongly reducing atmosphere maintained for a few hours at 1,600 to 1,700° F.

III. GENERAL SUMMARY, PARTS I, II, AND III

Efflorescence on face-brick walls may be due to soluble salts in cement, lime, or concrete materials wherever used in a wall, to common brick and hollow tile in the back-up materials, and to the harder burned face brick.

Many face brick, as well as mortar materials, contain a negligible amount of such soluble salts and are safe from the standpoint of efflorescence.

If a brick contains 0.05 per cent or less of water-soluble sulphuric anhydride in its outer one-eighth inch of exposed surface, it is not apt to contribute to the development of efflorescence on a wall under conditions most favorable for such development.

Such salts in the mortar materials which tend to appear on a wall surface under favorable conditions may be prevented from so appearing to a very considerable extent by the use of certain water-repellent substances. These substances should be well mixed with the mortar materials. The most effective of such water-repellent substances have been found to be ammonium or calcium stearates. Either of these materials should be added to mortars in an amount equal to 2 per cent by weight of the cement or of the lime, or of the cement plus lime in case both are used in the mortar.

Salts in brick which may contribute to the development of efflorescence on a wall are for the most part formed in the surfaces of the brick during the drying and burning operations.

The salts so formed in the surface of face brick are also the cause of kiln scum.

In order to reduce kiln scumming and any tendency in a face brick to develop efflorescence when laid in a wall, intelligent control of plant procedures is far more necessary and is also a far more economical means than is the use of barium compounds.

In order to reduce the extent of formation of sulphates in the drier, every controllable factor should be so adjusted as to insure the maximum rate of drying, at the same time keeping within the limits of safety as regards cracking.

The most desirable conditions to insure rapid drying, and hence a minimum of salts formed in the brick during this operation, are: (*a*) A low humidity, (*b*) a minimum amount of mixing water, (*c*) a relatively high temperature (212° F., if possible), and (*d*) good circulation of air or draft in all portions of the drying chamber.

The ideal condition is to admit none of the gaseous combustion products of sulphur into the drying chamber. This condition may be approached, if not actually realized, by exhausting the kiln for a period of time before connecting it to the drier if the waste-heat system of drying is used. It is necessary also to thoroughly rake out and clean all fire boxes before connecting a kiln to a drier. By observing this last-mentioned point a very annoying instance of scumming has been thoroughly checked in one plant after it had continued for a period of two months.

The period of water smoking should be shortened to the least possible length of time. A good draft will make such a method of procedure a safer one.

Increasing the draft is not as effective for rapid drying as increasing the heating rate. If there is an appreciable quantity of pyrite in the clay, the extent of soluble salt formation is increased by a rapid draft at the combustion temperature of pyrite.

It is hardly within the realm of possibility to decrease materially the extent of sulphate formation by attempting to find a coal low in sulphur content. Under favorable conditions for the formation of salts, decreasing the concentration of sulphur dioxide (the combustion product of sulphur) from 5 to 0.5 per cent by volume of the total kiln atmosphere accomplishes but very little.

If in order to produce a desired shade of face brick it is impossible to burn with a reducing atmosphere, the soaking period should be extended. The soaking temperature should be also increased as much as possible without altering the desired shade.

It is probable that reduction carried out at a temperature of from 1,600 to 1,750° F. may effect practically complete decomposition of the sulphates, and that by thereafter changing to an oxidizing atmosphere and continuing such during the entire soaking period the desired shade may be acquired and a brick free from scum and with no efflorescence-forming sulphates in it may be produced.

Dry-house or fixed scum is caused by soluble salts in clay. These salts are for the most part sulphates of sodium and potassium which melt before their decomposition is effected. They accumulate on the surface during slow drying and melt, become "fixed," during subsequent burning.

Dry-house scum may be reduced, if not altogether eliminated, by (*a*) rapid drying, (*b*) a strongly reducing atmosphere maintained at a temperature of from 1,600 to 1,700° F. (too low for these salts to melt), and (*c*) barium treatment of the clay.

Barium compounds are recommended when and only when dry-house or fixed scum is known to occur.

It is further recommended that for this purpose the more soluble compounds of barium rather than barium carbonate be used.

IV. ACKNOWLEDGMENTS

This investigation, which was sponsored by the American Face-Brick Association, was conducted at the National Bureau of Standards and in accordance with the research associate plan of the bureau.

Acknowledgment is made at this time of the very valuable suggestions received prior to and during the investigation from the members of the research committee of the association and also of those received from members of the ceramic division of the bureau. The cooperation and constructive criticisms of both of these organizations tended toward the acquisition of facts most relevant to the problem in the minimum length of time.

Washington, November 29, 1927.

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